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1,3-divinyl-tetramethyldisilyl chalcogenides.

Ankin. Vahradian
University of Windsor

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**LA THÈSE A ÉTÉ
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**1,3-DIVINYLTETRAMETHYLDISILYL
CHALCOGENIDES**



By
Ankin Vahradian

A Thesis

Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in partial fulfillment of the
requirements for the Degree of Master of Science
at the University of Windsor

Windsor, Ontario

1981

② Ankin Vahradian 1981

758116

To my wife,
and my parents.

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List of abbreviations

Me, methyl; Vin, vinyl or $\text{CH}_2=\text{CH}$; Bu, butyl; Ph, phenyl
v.p., vapour pressure; M, a group IV element
n.m.r., nuclear magnetic resonance; i.r. infrared;
R, Raman; p.p.m., parts per million
X, halogen; E, chalcogen; TMS, tetramethylsilane
 ν , stretch; δ , deformation; ρ , rock
R.T., room temperature

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ABSTRACT

The work in this thesis is concerned with the synthesis and characterization of some new vinyl-silyl species.

The synthetic route involves the metathetical exchange reactions of chlorovinyl dimethylsilane with the corresponding dilithium salts, Li_2E ($\text{E}=\text{O}, \text{S}, \text{Se}, \text{Te}$), which yield the corresponding $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$. The products were characterized by the usual spectroscopic methods, i.e. ^1H n.m.r. and Raman, as well as by mass spectrometry where appropriate.

The reactivity of 1,3-divinyl-tetramethyldisilyl chalcogenides was studied by reacting them with some simple species such as HCl , HBr , aqueous HCN , SO_2F_2 , CCl_3SCl , CH_3SH , H_2S and H_2Se .

Some of the spectroscopic features of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ were compared with those of some related species such as $(\text{HSiMe}_2)_2\text{E}$ and $(\text{SiMe}_3)_2\text{E}$.

Partial halogenation reactions of some silanes and germanes were also carried out not only for the spectroscopic interest in the products, but also for their importance and utility in the synthesis of new silyl and germyl species.

CHAPTER I

EXPERIMENTAL TECHNIQUES

Halogeno-silanes and -germanes are among the most important intermediates in the synthesis of various silyl and germyl derivatives.

The reactivity of the functional groups is primarily affected by the nature and extent of the organic substituent at the silicon or germanium atom.

In conformity with their volatile nature , sensitivity to hydrolysis , and disagreeable odour , it was necessary to pay careful attention to the design of "gas-liquid" or "solid" handling equipment. Vacuum line techniques¹⁻⁴, both for the preparation and transfer of the material , were of extreme importance. Where certain off-the-line procedures were required , the chemicals and equipment were handled in a nitrogen-filled glove bag.

I.1 THE VACUUM LINE

The vacuum line (Fig. I.1) was constructed with Pyrex glass; it consisted of two manifolds (B,B') (volume ca . 150 ml each). Manifolds (B) and (B') were interconnected by four "U"-traps , and a central manifold (C) leading to two liquid nitrogen backing traps (E) , a mercury diffusion pump (F) , and a rotary oil pump (G). Pressure readings between 1-760 Torr (0.13-101.33 kPa) were monitored by the mercury manometers (A,A') (± 0.5 Torr); usual pressure readings recorded

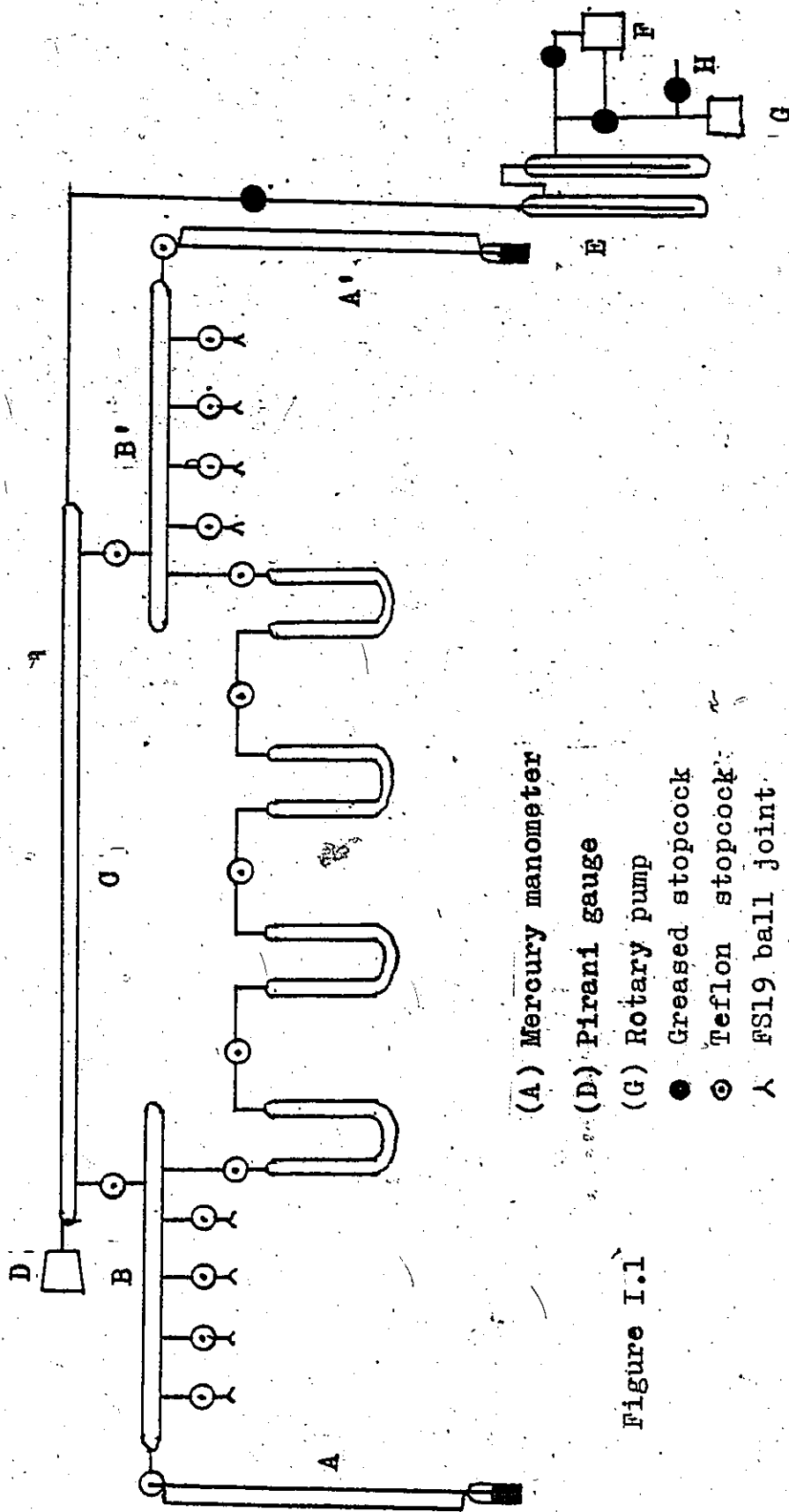


Figure I.1

were 1.5×10^{-2} Torr or 2×10^{-3} kPa. Pressure readings below 1 Torr (0.13 kPa) were recorded by a Pirani vacuum gauge (D). Because of the marked solubility of the compounds in hydrocarbon grease, high-vacuum Teflon-in-glass stopcocks and silicon-greased ground glass joints were utilized.

I.2 THE SEPARATION OF VOLATILE MATERIALS

The separation of volatile materials in the vacuum line was accomplished by trap-to-trap distillation using low temperature slush baths^{1,4}. Table I.1 lists

Table I.1 Low temperature slush baths

| Material | Slush temp. (°C) |
|--|------------------|
| ice/water | 0 |
| ice/salt water | 0 to -15 |
| carbon tetrachloride/liquid N ₂ | -23 |
| chlorobenzene/liquid N ₂ | -45 |
| chloroform/liquid N ₂ | -63 |
| 'dry-ice'/acetone (or methanol) | -78 |
| toluene/liquid N ₂ | -96 |
| 1-bromobutane/liquid N ₂ | -112 |
| methyl cyclohexane/liquid N ₂ | -126 |
| n-pentane/liquid N ₂ | -132 |
| iso-pentane/liquid N ₂ | -160 |
| liquid N ₂ | -196 |

* All slush bath temperatures are estimated to $\pm 5^{\circ}\text{C}$.

the slush baths and their corresponding temperatures. The efficiency of separating two or more compounds depends upon the difference of their vapour pressures at different temperatures, the efficiency of the vacuum system, the quantity and relative composition of the mixture, and the rate of distillation. After one or more fractional condensations the purity of the separated compounds was confirmed by spectroscopic analysis.

I.3 STORAGE AND REACTION VESSELS

The storage and reaction vessels used in this work are shown in Figure I.2. These were constructed of Pyrex-glass. The type of vessel used was determined by the stability, volatility and quantity of the substance in question, while experimental conditions, and the nature of the compound determined the type of stopcock fitted on the reaction or storage vessel.

Solid phase reactions in a solvent were conducted in vessel (A) (e.g. the reaction of lithium and arsenic in ammonia). Vessel (A) was modified to vessel (B) as shown in the diagram, in order to be used as a storage vessel for compounds with very low volatility such as $(\text{VInSiMe}_2)_2\text{Te}$. Vessel (C) was used as a storage vessel for simple hydrides and gases that

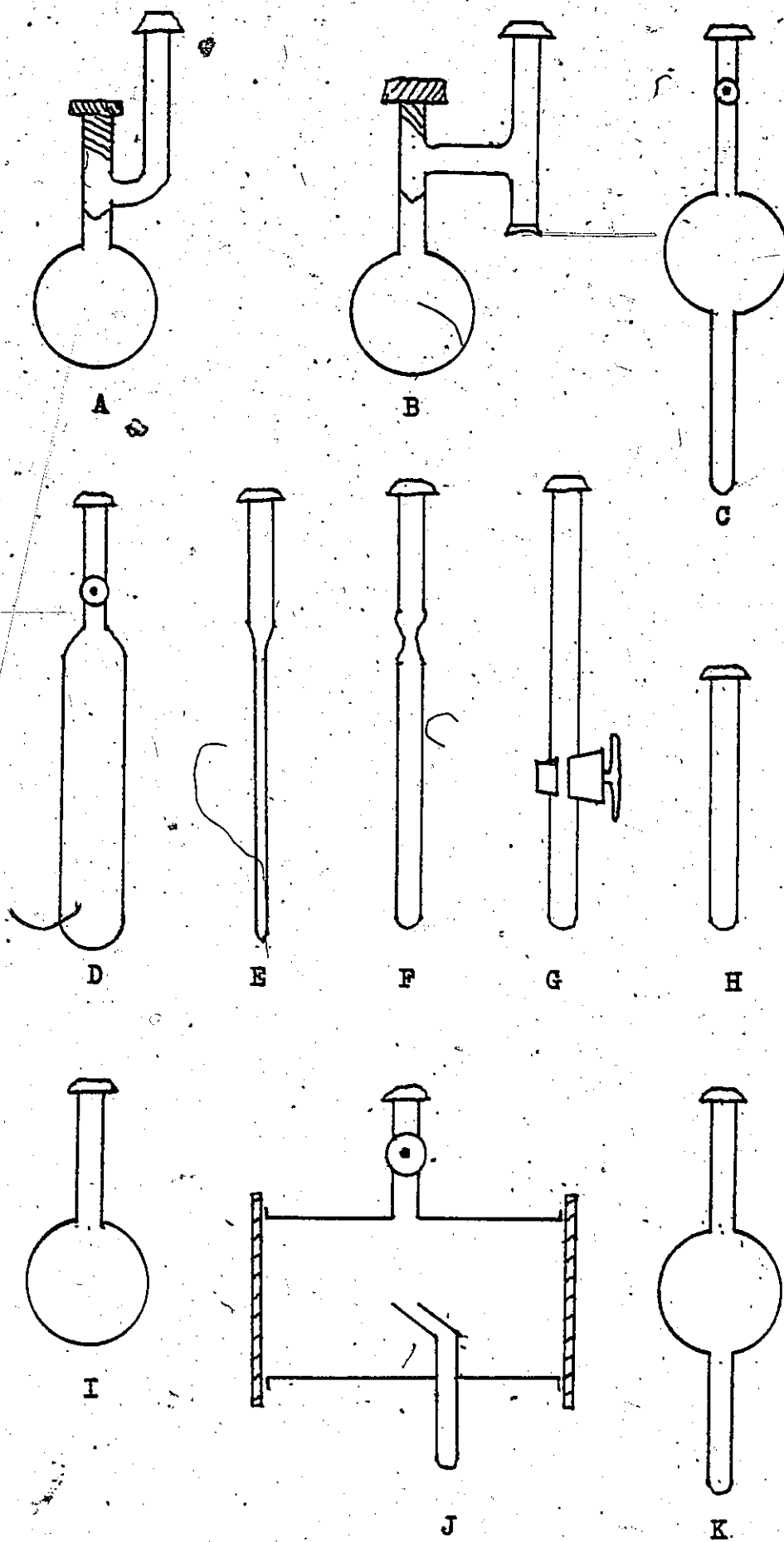


Figure I.2

are stable at R.T. (e.g. SiH_4 , GeH_4 , HCl , H_2S). Low volatile liquids were stored in vessel (D) (e.g. $\text{VinSiMe}_2\text{Cl}$, BCl_3). Vessel (E) (1-4 mm o.d.) was used for sealed tube reactions and for sampling compounds to be utilized for spectroscopic analysis (e.g. raman , n.m.r.). For sealing these tubes , a sharp hot flame was used with an appropriate torch , and the flame was localized in a small area. When a compound has to be kept indefinitely for future use or when it is particularly unstable , it is best to keep it in a sealed tube at a temperature below that of R.T. A glass tube (5 mm o.d.) is attached to a MS 19 ball joint with a constriction at the neck (F) , thus facilitating the process of sealing the tube. Furthermore , the use of vessel (F) reduces the use of expensive stopcocks. Opening of sealed tubes on the vacuum line was accomplished with the tube breaker (G). For small scale reactions at low pressures or in the condensed phase , a finger (H) (5-100 ml) fitted with a MS 19 ball joint and a Teflon-in-glass stopcock was used. Vessel (I) , fitted with a MS 19 ball joint and an appropriate stopcock , was used to store dry solvents (e.g. Et_2O) under vacuum and in contact with a drying agent such as $\text{Li}[\text{AlH}_4]$. Vessel (K) was used for gas phase reactions.

I.4 CLEANING OF RE-USABLE GLASSWARE

The thorough cleaning of re-usable glassware is very important in a laboratory, because not only does it reduce waste but also it saves a considerable amount of time. For example, many reactive compounds, if stored in thoroughly clean vessels will not decompose, but their decomposition is apparently catalysed by traces of foreign material. The cleaning of glassware was achieved through such reagents as water, 10% HF, $\text{HCl}:\text{HNO}_3$ 3:1, NaOH/ethanolic solution, organic solvents, detergents, etc. Soaking and washing with a brush was found to be a very effective method in achieving the desired results. It cannot be overemphasized that efficient cleaning is no small matter when dealing with compounds such as volatile selenium and tellurium species that readily deposit metallic films that adhere strongly. After cleaning, the glassware was dried in an oven at 100°C .

I.5 INSTRUMENTATION AND PHYSICAL METHODS

(a) Infrared spectroscopy: Infrared spectra were recorded on Beckman I.R. 12 ($4000\text{--}200\text{ cm}^{-1}$) and Perkin-Elmer 180 Recorder Console spectrometers; using a 9 cm gas cell (Fig. I.2 J) equipped with KBr windows. A small finger, sealed into the front side of the cell, permitted distillation of small quantities of material into the cell. Gas pressures ranging from 1 to 15 Torr

were usually used. Low volatile liquids were recorded as smears between two CsI or KBr plates in an air tight device. Polyethylene plates were used when recording far-i.r. spectra. The positions of sharp peaks were accurate to $\pm 1 \text{ cm}^{-1}$.

(b) Raman spectroscopy: Raman spectra were recorded on a Spectra Physics/Beckman 700 Laser-Raman spectrometer using the 5145 Å excitation of an argon ion laser. The samples were sealed under vacuum in Pyrex glass capillaries (ca. 50-100 mm long; ca. 2 mm o.d.) and polarization measurements were carried out by examining the spectrum with incident light respectively parallel and perpendicular to the axis of a polaroid analyzer. The depolarization values thus obtained were directly proportional to the true values. Accuracies of $\pm 2 \text{ cm}^{-1}$ were routinely obtained on sharp peaks. The important peaks were expanded to give frequencies accurate to $\pm 0.5 \text{ cm}^{-1}$.

(c) Nuclear magnetic resonance spectroscopy
(^1H n.m.r. and ^{13}C n.m.r.): The proton spectra were recorded on a JEOL C-60HL spectrometer operating at a resonance frequency of 60 MHz at R.T. Chemical shifts are given in p.p.m. ($\delta \pm 0.02 \text{ p.p.m.}$) to low field of internal TMS in CCl_4 solution (5%V/V). Chemical shifts were also measured relative to cyclo-

hexane where appropriate. Deviations for coupling constants of neat liquids were $J(\text{HH}) \pm 0.05 \text{ Hz}$, $J(\text{CH}) \pm 0.20 \text{ Hz}$. The carbon-13 spectra were obtained on a Bruker CPX 100 (FT model) spectrometer, operating at a resonance frequency of 22.639 MHz, at a probe temperature of 35°C. All spectra were recorded under ^1H noise-decoupling conditions. The samples were sealed in capillaries (ca. 2 mm o.d.) as neat liquids or in cyclohexane solution, and the capillaries were placed coaxially in 5 mm tubes containing tetramethylsilane (TMS) as a standard and CDCl_3 (CCl_4 for proton spectra, to ensure good sample spinning) which served as a lock.

(d) Mass spectrometry: The mass spectra were obtained on a Varian MAT CH5 double focusing spectrometer, equipped with an INCOS 2000 computer system. The spectra were recorded at 70 eV. Molecular ions were also obtained using field ionization techniques where appropriate. The samples were admitted into the spectrometer from a small finger with a 3 mm Teflon-in-glass stopcock. Sealed tubes were broken using a tube breaker (Fig. I.2G) on a small vacuum line connected to the inlet system of the spectrometer.

(e) Vapour pressures: The vapour pressures of the various species under investigation were obtained by allowing them to expand against a mercury manometer.

CHAPTER II

THE PREPARATION AND PURIFICATION OF STARTING

MATERIALS

The following compounds were obtained either through commercial sources, or were prepared by known synthetic procedures. As the synthesis of these compounds was not of primary interest, they are considered 'starting materials'. The purity of these materials was confirmed spectroscopically or by vapour pressure measurements (V.P.) where appropriate.

ALUMINIUM, Al: commercial^d; used as obtained.

ALUMINIUM TRIIODIDE, AlI₃: commercial^b; stored under N₂ at R.T.; resublimed and dried under vacuum.¹

AMMONIA, NH₃: commercial^g; pumped off under vacuum through a trap held at -78° and dried over sodium or lithium.

ANTIMONY TRIFLUORIDE, SbF₃: commercialⁱ; dried in a 65° oven for five hours or longer before use.

ANTIMONY PENTACHLORIDE, SbCl₅: commercial^e; used as obtained.

ARSENIC, As: commercial^b; used as obtained.

BORON TRICHLORIDE, BCl₃: commercial^g; degassed at -112° prior to use and stored at R.T. in vessel 'D' fitted with a Teflon-in-glass stopcock; i.r.⁵.

BROMOTRIMETHYLGERMANE, Me₃GeBr: commercially available^b; degassed at -78° and stored in vessel 'D' at R.T.; i.r.⁶; n.m.r.^{7,8}

BROMOTRIMETHYLSILANE, Me₃SiBr: commercially available^{jk}; degassed at -78° before use and stored at R.T.

in vessel 'D' ; i.r.^{9,10} , n.m.r.¹¹

CHLORODIMETHYLVINYLSILANE , $\text{CH}_2=\text{CHSiMe}_2\text{Cl}$: commercial-
ly available^k; degassed at -78° and stored at R.T. in
vessel 'D' ; i.r./R¹² , n.m.r.¹³

CHLOROTRIMETHYLSILANE , Me_3SiCl : commercially avail-
able^b; distilled through traps held at -45° , -78° , and
 -196° . The pure Me_3SiCl was condensed in the -78° trap
and stored at R.T. in vessel 'D' ; i.r.¹⁴ , n.m.r.¹¹ ,
v.p.¹

DICHLORODIMETHYLGERMANE , Me_2GeCl_2 : commercially avail-
able^b; degassed at -78° and stored in vessel 'D' at R.T. ;
i.r./R^{15,18} , n.m.r.¹⁵

GERMANE , GeH_4 : commercially available^g; purified by
passage through traps held at -126° and degassed at
 -196° . Stored at R.T. in vessel 'C' ; i.r.¹⁶ , n.m.r.¹⁷ ,
v.p.¹

HEXAMETHYLDISILANE , $\text{Me}_3\text{SiSiMe}_3$: commercially avail-
able^k; degassed at -78° and stored at R.T. ; i.r./R^{19,20} ,
n.m.r.²¹

HYDROGEN CHLORIDE , HCl : commercially available^g; de-
gassed at -196° and stored in vessel 'C' at R.T. ; i.r.²²

HYDROGEN IODIDE , HI : hydrogen iodide was prepared in
the following manner²³. A reaction vessel (ca. 250 ml ,
type 'I') fitted with a stirring bar and a dropping fun-
nel was charged with red phosphorus (10g) or with phos-

phorus pentoxide (40g). In order to reduce contamination of the vacuum line by iodine vapour, the adaptor to the vacuum line was plugged with glass wool. After thoroughly evacuating the system, a solution consisting of iodine (4g) and hydroiodic acid (80g or ca. 50ml) was added in drops. The reaction was carried out at R.T. The reaction products were passed through traps held in series at -23° , -78° , and -196° . Pure HI was collected in the -196° trap. Stored at R.T. in vessel 'D'; i.r.²²

HYDROGEN SELENIDE, H_2Se AND D_2Se : hydrogen selenide was prepared in the following manner²⁴. A finely powdered mixture of aluminium (3.3 g) and selenium (5.6 g) was placed in a small crucible, and a strip of burning magnesium^d ribbon was plunged into it in order to form Al_2Se_3 . After cooling, the products and the crucible were placed in a reaction vessel fitted with a dropping funnel and an adaptor, in order to be able to attach it to the vacuum line. After evacuating the system, distilled water, H_2O or D_2O , was slowly added into the reaction vessel. H_2Se was immediately formed, and after passing it through a trap held at -78° it was collected in another trap held at -196° . Thereafter it was stored at R.T. in vessel 'C'.

HYDROGEN SULPHIDE, H_2S AND D_2S : prepared²⁵ by an analogous procedure to that for H_2Se , and stored in vessel 'C'

at R.T.

IODINE , I_2 : commercially available^d; resublimed and degassed at -78° before use.

IODOGERMANE , H_3GeI : prepared²⁶ by the reaction of germane with iodine , stored at -78° or -196° in vessel 'D'. Accidental explosions of the reaction carried out in sealed tubes were avoided by using reaction vessels equipped with Teflon-in-glass stopcocks.

LEAD (II) OXIDE , PbO : commercially available^b; used as obtained.

LITHIUM , Li : commercially available^b; cleaned with petroleum ether before use.

LITHIUM ALUMINIUM HYDRIDE , $Li[AlH_4]$: commercially available^b; used as supplied.

LITHIUM OXIDE , Li_2O : commercially available^b; used as supplied.

LITHIUM SULPHIDE , Li_2S : commercially available^b or prepared from the elements in liquid ammonia²⁷.

METHANETHIOL , CH_3SH : commercially available^a; degassed at -196° prior to use ; stored at R.T. in vessel 'D' ; i.r.²²

SELENIUM , Se_8 : commercially available^d; used as supplied.

SILANE , SiH_4 : commercially available^g; degassed at -196° and stored at R.T.; i.r.¹⁶, n.m.r.²⁸

SOLVENTS : dimethyl ether^g was used as supplied .
 Diethyl ether^e and n-butyl ether^a were dried and
 stored over $\text{Li}[\text{AlH}_4]$ in vessel 'I' at R.T. prior
 to use. Spectral grade^{c,h} carbon tetrachloride and
 cyclohexane were vacuum distilled and stored in ves-
 sel 'D' at R.T.

SULPHUR , S_8 : commercially available^e; used as sup-
 plied.

TELLURIUM POWDER , Te : commercially available^d; used
 as supplied.

TETRAMETHYLSILANE , Me_4Si : commercially available^f;
 stored in vessel 'D' at R.T. ; n.m.r.²⁹

COMMERCIAL SUPPLIES

- a. Aldrich Chemical Co. , Milwaukee , Wisc.
- b. Alfa Inorganics Inc. , Beverly , Mass.
- c. Anachemia Chemicals Ltd. , Montreal , P.Q.
- d. The British Drug Houses Ltd. , Poole , Dorset , U.K.
- e. Fisher Scientific Co. , Fair Lawn , N.J.
- f. Laramie Chemical Co. , Laramie , Wy.
- g. Matheson Gas Products , East Rutherford , N.J.
- h. NMR Specialties Inc. , New Kensington , Pa.
- i. Ozark-Mahoning Co. , Tulsa , Okla.
- j. PCR Inc. , Gainesville , Fla.
- k. Petrarch Systems , Levittown , Pa.

CHAPTER III

THE SYNTHESIS OF

1,3-DIVINYLTETRAMETHYLDISILYL

CHALCOGENIDES

III.1 INTRODUCTION

(a) The nature of the silicon atom: Silicon is a member of Group IV in the periodic table, sharing this position with carbon, germanium, tin, and lead. As is well known, carbon ($1s^2, 2s^2, 2p^2$) commonly forms four single covalent bonds and can be considered as undergoing sp^3 hybridization with its orbitals directed towards the corners of a tetrahedron. Similarly, although the second row element silicon ($[Ne] 3s^2, 3p^2, 3d^0$) has nine orbitals of its M shell available for bonding, it nevertheless generally prefers to utilize only four of its valence orbitals in bonding. This is because the 3s and 3p orbitals are energetically more stable than the 3d orbital. Thus, the concept of sp^3 hybridization in silicon and its subgroup can still be used to rationalize the same tetrahedral bonding as in carbon.³⁰ Differences in the properties which give silicon (and its subgroup) its distinctive feature, and serve to differentiate it from carbon, may be rationalized by accounting for two fundamental features. First, silicon's filled L-shell shields its valence orbitals from attractive nuclear forces to a greater extent than that of carbon's K-shell. Thus, the valence electrons in silicon are lost more readily than those in carbon, and silicon is said to be more electro-

positive than carbon. Therefore , many silicon bonds have a rather high ionic character (Table III.1).

This fact explains why silicon-oxygen and silicon-halogen bonds undergo heterolytic fission so readily , and their failure to rupture homolytically at high temperature³¹. By contrast , the bond energy of the C-Si bond ($76.0 \text{ Kcal mol}^{-1}$) is somewhat lower than the C-C value ($82.6 \text{ Kcal mol}^{-1}$). Similarly, the difference between the Si-H ($76.0 \text{ Kcal mol}^{-1}$) and the C-H bond ($98.8 \text{ Kcal mol}^{-1}$) is even greater . Furthermore , because silicon is more electropositive than either carbon or hydrogen , ionic fission of these bonds always proceeds by nucleophilic attack directly on silicon, and by electrophilic attack on its partner , or by a more or less concerted mechanism.

Silicon has a second distinctive feature , which arises from its second row position in Group IV of the periodic table. It has relatively low-lying empty 3d orbitals , which may be utilized in chemical bonding. These empty d-orbitals may be utilized in the formation of sp^3d and sp^3d^2 hybridization. Silicon , however , is thought to never utilize more than two of these d-orbitals , hence the coordination number never exceeds six^{31,32}. In the nd-orbital hypothesis the appearance of π -acceptor properties of M (M=Group

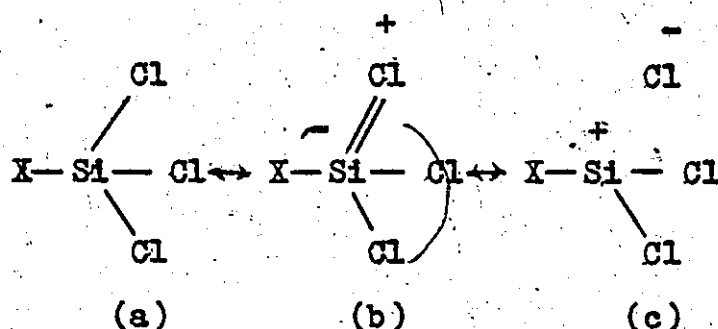
Table III.1 Selected parameters of various silicon and carbon bonds.*

| Atom | Electroneg. of Z | Ionicity of Si-Z % | Bond energy of Si-Z Kcal mol ⁻¹ | Ionicity of C-Z % | Bond energy of C-Z Kcal mol ⁻¹ |
|------|---------------------|--------------------------|---|-------------------------|--|
| Si | 1.8 | 0 | 53 | 12 | 76.0 |
| H | 2.1 | 2 | 76 | 4 | 98.8 |
| C | 2.5 | 12 | 76 | 0 | 82.6 |
| O | 3.5 | 50 | 108 | 22 | 85.5 |
| N | 3.0 | 30 | 77 | 7 | 72.8 |
| S | 2.5 | 12 | 70 | 0 | - |
| F | 4.0 | 70 | 135 | 43 | 116.0 |
| Cl | 3.0 | 30 | 91 | 7 | 81.0 |
| Br | 2.8 | 22 | 74 | 2 | 68.0 |
| I | 2.5 | 8 | 56 | 0 | 51.0 |

*Reference 33

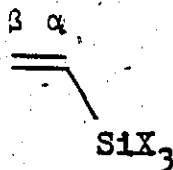
IV elements) is the result of partial transfer of lone pair(s) or π -electrons of X (X=an atom with lone pair(s) or an unsaturated group) to the nd-orbitals of M ($p \rightarrow d$) π interaction. The ability of the substituent X to form ($p \rightarrow d$) π M-X bonds is known to be proportional to the resonance constants δ_R of the substituent. In this respect, resonance hybrids, such as (a)-(c) shown

below , have been proposed to account for the shorten-

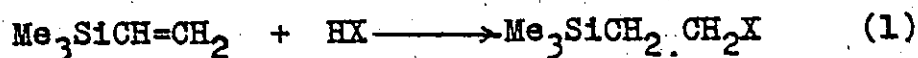


ing of the Si-X bond length , compared to the calculated value³⁴. However , the relationship between the resonance concept and the view of a $(p \rightarrow d)\pi$ bond is complicated by the polarity of the σ -bond , which , in addition to exerting a direct influence on the π -orbitals , brings about changes in the hybridization of the σ -bonding orbitals. Nevertheless , the larger the halogen atom the less the amount of $(p \rightarrow d)\pi$ bonding , possibly because of increasingly poorer overlap^{35 , 36}. Replacement of the Si atom by Ge leads to less appreciable $(p \rightarrow d)\pi$ interaction , presumably , in part due to the presence of a radial node in the 4d orbitals³⁷. The linking of vinyl groups to the silicon atom leads to such a class of compounds , wherein the α -carbon of the vinyl group is analogous to the ipso carbon of the phenyl ring , and the vinyl β -carbon is related to the ortho phenyl carbon in the corres-

ponding PhX compounds, e.g.



The earlier research of silyl species containing phenyl or vinyl groups has been motivated by the need for polymeric materials of greater thermal stability than the conventional organic polymers. Added motivation however, for research in the vinyl-metal field came from the increasing interest in chemical bonding in organometallic compounds. Chemical evidence for (p→d) π bonding between silicon and a vinyl group has been inferred from anti-Markownikoff rule of addition of hydrogen halides to vinyltrimethylsilane³⁰, i.e.



The positive inductive effect of the Me_3Si group which operates in favour of the Markownikoff rule, i.e.

$\text{Me}_3\text{Si}^{\delta+} \quad \text{CH}=\text{CH}_2^{\delta-}$ is outweighed by the participation of the π -electrons of the vinyl group in the d-orbitals of silicon, i.e. $\text{Me}_3\text{Si}^{\delta-} \leftarrow \text{CH}=\text{CH}_2^{\delta+}$. However,

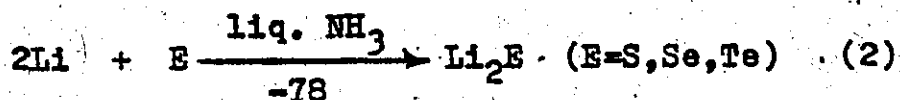
the latter effect can be overcompensated by the positive inductive effect of a methyl group in the α -position, $\text{Me}_3\text{SiC}(\text{Me})=\text{CH}_2$, so that the addition of hydrogen halides yields products with Markownikoff's orientation $\text{Me}_3\text{SiCClMe}_2$ ³⁸. This implies that the Si-C bond, which possesses partial double bond character is even capable of participating in conjugation, otherwise it would hardly be possible to explain the anti-Markownikoff addition of organolithium compounds to triphenylvinylsilane, which occurs only with highly conjugated systems³⁹. Replacement of a methyl group by siloxy groups leading to vinylmethyilsiloxane is reflected in the reactivity of the heavy atom skeleton $\text{C}=\text{C}-\text{Si}-\text{O}$. Namely, the reactivity is the result of at least three mechanistic effects: (a) weakening of the positive inductive effect of the silyl group, (b) $(p \rightarrow d)\pi$ interaction between silicon and the vinyl group, and (c) competitive $(p \rightarrow d)\pi$ conjugation of silicon with the two electron pairs of oxygen. The operation of the latter effect has been shown by the increased reactivity of the double bond in 3-vinylheptamethyltrisiloxane as compared with that in vinyl pentamethyldisiloxane, as a result of the weakening of the original $(p \rightarrow d)\pi$ bond between the vinyl group and silicon⁴⁰. Similar conclusions

have been reached on the basis of infrared and nuclear magnetic studies^{41,42}.

In order to better understand the effect of the silicon atom upon the behaviour of a proximate organic functional group and vice versa, a systematic study of unexplored organosilyl groups linked to a Group IV element was undertaken. Thus the present chapter describes the preparation of a series of bis(vinyldimethylsilyl) chalcogenides; (1,3-divinyl-tetramethyldisilyl chalcogenides); $(\text{VinMe}_2\text{Si})_2\text{E}$ where $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{Vin} = -\text{CH}=\text{CH}_2$, and their spectroscopic characterization. The synthetic route involves the metathetical reactions of chlorevinyl dimethylsilane with the corresponding dilithium salt, Li_2E . The siloxane $(\text{VinMe}_2\text{Si})_2\text{O}$, the only known compound⁴³ of this series, was readily prepared by the hydrolysis of $\text{VinMe}_2\text{SiCl}$. While $\text{VinMe}_2\text{SiCl}$ was commercially available, the dilithium salts Li_2E ($\text{E} = \text{S}, \text{Se}, \text{Te}$) were prepared from the elements in liquid ammonia. Spectral evidence was sought for tentative structural assignments of the title compounds by examining the infrared, Raman, ^1H and ^{13}C n.m.r. spectroscopic features, as well as the mass spectra where appropriate.

III.2 EXPERIMENTAL

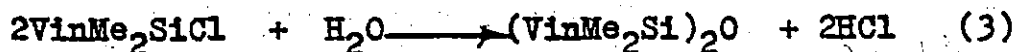
(a) Preparation of dilithium chalcogenides



In a typical experiment the reaction vessel was a bulb (volume about 70 ml) the neck of which was extended into a tube (ca. 10 cm ; 10 mm o.d.) terminating in a high-vacuum Teflon-in-glass stopcock and glass joint for attachment to the vacuum line. The reactor was evacuated and purged with dry nitrogen.⁹ The stopcock plug was removed in a dry box, and clean lithium wire (0.0694 g ; 10.00 mmol), powdered selenium (0.3960 g ; 5.02 mmol), and a small magnetic stirring bar were added to the reactor. The stopcock was replaced and the vessel was then thoroughly evacuated on the vacuum line. Dry ammonia⁴⁴ (about 12 ml) was then distilled into the vessel held at -196°. The stopcock was closed and the reaction mixture was allowed to stand at -78° with occasional shaking until the blue colour of dissolved lithium was discharged (about 10-12 hours). This was slower if the lithium wire had an oxide coating. With frequent cautious warming and shaking, while monitoring the pressure of the ammonia, the reaction time could be decreased greatly. Upon completion of the reaction the ammonia was distilled out of the reactor under vacuum and the residual solid was heated to 150-155° in vacuo for

5-6 hours. The dilithium selenide⁴⁵ thus prepared is light grey and should show no signs of residual lithium or selenium ; polyselenides impart a characteristic red colour to the material. Hydrolysis gave typically 98% of the selenium content required for Li_2Se as H_2Se . The dilithium telluride^{45,46} was prepared in a similar manner from lithium wire (0.0694 g ; 10 mmol) and powdered tellurium (0.6390 g ; 5.01 mmol). It is characteristically a darker grey than the selenide , it appeared homogeneous. Dilithium sulphide²⁷ , available commercially , was found to contain dilithium oxide , and hence it was prepared as above from lithium wire (0.0694 g ; 10 mmol) and sulphur powder (0.162 g ; 5.05 mmol). It is a characteristically yellow compound , which slowly hydrolyzes to Li_2O and H_2S . Hence the dilithium salts were stored under nitrogen at R.T.

(b) Reaction of chlorodimethylvinylsilane
with water



Typically , $\text{VinMe}_2\text{SiCl}$ (5.37 mmol) was condensed, under vacuum conditions , into a reaction tube (ca. 20 ml) containing 8 ml of degassed distilled water.

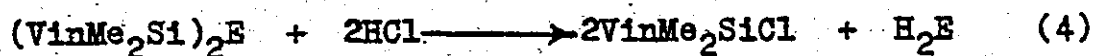
The stopcock was closed and the contents were allowed to react at R.T. with occasional shaking. After about 40 minutes the volatile material was distilled through a series of 'U'-traps held at -23° , -45° , and -196° . The trap at -23° retained the excess water, while that at -45° contained $(\text{VinMe}_2\text{Si})_2\text{O}$. Traces of $(\text{VinMe}_2\text{Si})_2\text{O}$ were also collected in the trap at -196° , and the amount increased with longer fractionation time and back pumping. The fraction at -45° was then collected in a storage vessel, and then passed through a loosely packed tube with small amounts of phosphorus V oxide supported on glass wool. Double passes of the oxide through P_4O_{10} afforded complete removal of the water as indicated by the absence of $\nu(\text{OH})$ in the infrared spectrum. In the presence of larger amounts of P_4O_{10} it appears that $(\text{VinMe}_2\text{Si})_2\text{O}$ reacts with P_4O_{10} to form presumably phosphates of the type $(\text{VinMe}_2\text{Si})_3\text{PO}_4$ and/or $(-\text{PO}_3\text{SiMe}_2\text{Vin}-)_n^{47,48}$. The yield of $(\text{VinMe}_2\text{Si})_2\text{O}$, based on the $\text{VinMe}_2\text{SiCl}$ consumed, was 89%. Informative identification of $(\text{VinMe}_2\text{Si})_2\text{O}$ was obtained from the mass spectrum, which gave the major peak at m/e 171 (100%) $(\text{C}_7\text{H}_{15}\text{Si}_2\text{O})^+$ corresponding to homolytic cleavage of methyl groups from the molecular ion P^+-CH_3 .

(c) Reaction of $\text{VinMe}_2\text{SiCl}$ with dilithium sulphide, selenide, and telluride

Diethyl ether (ca. 15 ml) and $\text{VinMe}_2\text{SiCl}$ (1.807 g ; 15 mmol) were distilled in vacuo into the reaction vessel held at -196° and containing dilithium selenide (ca. 8.00 mmol) prepared as above. The mixture was allowed to warm to R.T. and stirred for about seventy hours. After this time the volatile material was distilled in vacuo out of the reactor and fractionated through traps held at -45° and -196° . Diethyl ether and traces of unreacted $\text{VinMe}_2\text{SiCl}$ were identified in the -196° trap. The contents of the trap that was maintained at -45° were redistilled through traps held in series at -23° , -45° , and -196° . The former trap retained pure bis(vinyldimethylsilyl) selenide $[(\text{VinMe}_2\text{Si})_2\text{Se}$, 3.80 mmol , 80% yield] . Bis(vinyldimethylsilyl)oxide was found in the trap held at -45° (identified by the characteristic strong band at 1049 cm^{-1} in the i.r. spectrum of the gas). High yields of bis(vinyldimethylsilyl)telluride $(\text{VinMe}_2\text{Si})_2\text{Te}$, in the range of 70-85% were obtained by an analogous procedure using Li_2Te (ca. 6.00 mmol), diethyl ether (ca. 15 ml) and $\text{VinMe}_2\text{SiCl}$ (10.50 mmol). Yields of 85-90% of bis(vinyldimethylsilyl) sulphide were analogously obtained using Li_2S (ca. 5.00 mmol) , diethyl ether (ca. 15 ml) and $\text{VinMe}_2\text{SiCl}$ (10.00 mmol).

(d) Reaction of $(\text{VinMe}_2\text{Si})_2\text{E}$ E = S , Se , Te
with HCl

The reaction of bis(vinyldimethylsilyl)chalcogenides with an excess of gaseous hydrogen chloride indicated the protolytic cleavage of the S-E (E=S, Se, Te) bond.



Typically, $(\text{VinMe}_2\text{Si})_2\text{S}$ (1.25 mmol) and HCl (3.20 mmol) were condensed in vacuo into a small vessel (ca. 30 ml; type 'D', equipped with a Teflon-in-glass stopcock) held at -196° . The reactants were then allowed to warm to R.T. for about 30 minutes. After this time the products were fractionally distilled through a series of traps held at -78° and -196° . $\text{VinMe}_2\text{SiCl}$ was recovered in the former trap (2.40 mmol; 92% yield), identified by ^1H n.m.r.¹³ and vibrational¹² spectroscopy. H_2S and unreacted HCl were condensed into the latter trap. HCl was identified by vibrational²² spectroscopy, the products of this reaction provided an indirect evidence for the monomeric nature of $(\text{VinMe}_2\text{Si})_2\text{E}$ where E=S, Se, Te.

III.3 PHYSICAL PROPERTIES

Bis(vinyldimethylsilyl) chalcogenides are all liquids, the oxide and the sulphide are clear colourless liquids, while the selenide is pale yellow, and the telluride is very deep yellow or gold in colour. The sulphide, selenide, and telluride are of lower volatility than the oxide, with revolting

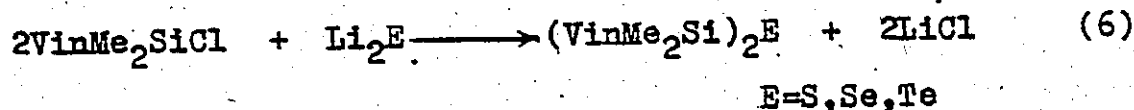
and persisting odours. Their volatility is sufficient that they could be easily handled under vacuum conditions, provided contact with silicon-grease was kept to a minimum. They are very easily oxidized upon exposure to air or moisture, with the liberation of hydrogen chalcogenide, H_2E ($E=S, Se, Te$). They are stable at R.T. and all the chalcogenides were kept in sealed tubes.

III.4 DISCUSSION

Exchange reactions of type (5) represent one of the most widely encountered types of chemical transformations, characteristic of inorganic, organic, and organometallic compounds, e.g.



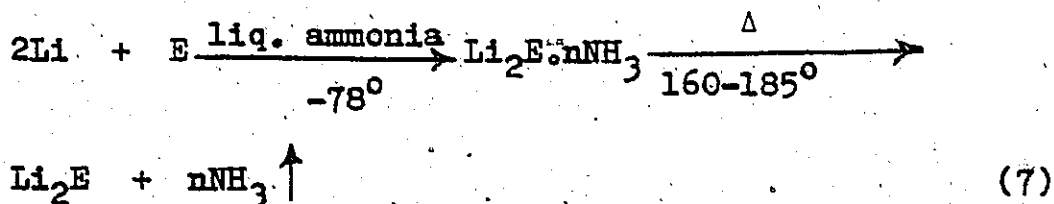
The use of this type of metathesis between Group IV halides and dilithium salts has been demonstrated previously for the synthesis of a number of disilyl and digermyl chalcogenides^{49,50}, $(Me_{3-n}H_nM)_2E$ where $M=Si, Ge$; $E=O, S, Se, Te$; $n=0 \rightarrow 3$. In this study this approach was extended to the synthesis of otherwise inaccessible vinyl-containing species, i.e.



The reactions were carried out at R.T. in diethyl ether as solvent. Upon the basis of the observed material balance the yields of the products are high (ca. 80-90%), and the only significant loss of material was due to the susceptible nature of the Si-Cl and Si-E bond to hydrolysis. The presence of disilazane $(\text{VinMe}_2\text{Si})_2\text{NH}$ was often observed in the mass spectrum in cases where the dilithium salt contained ammonia. e.g.

$$\left[\begin{array}{l} \text{P m/e 161 } (\text{Me}_6\text{Si}_2\text{NH})^+ \text{ 5\% , P-CH}_3 \text{ m/e 146} \\ (\text{Me}_5\text{Si}_2\text{NH})^+ \text{ 100\%} \end{array} \right]$$

The use of a slight excess of chalcogen and removal of solvated ammonia from Li_2E (7) resulted in complete conversion of $\text{VinMe}_2\text{SiCl}$ into the corresponding Si-E species. The oxide, $(\text{VinMe}_2\text{Si})_2\text{O}$ was readily obtained.



by the hydrolysis of the chloride. The ease of its formation is, in part, to be found in the exceptionally high Si-O thermochemical bond energy. Another way

of obtaining $(\text{VinMe}_2\text{Si})_2\text{O}$ is by the reaction between Li_2O and $\text{VinMe}_2\text{SiCl}$ in diethyl ether. Structural characterization of all the chalcogenides was obtained by ^1H and ^{13}C n.m.r. and vibrational spectroscopy and, in the case of the oxide, from its electron impact mass spectrum.

CHAPTER IV

THE CHARACTERIZATION OF

1,3-DIVINYLTETRAMETHYLDISILYL CHALCOGENIDES

$(\text{VinMe}_2\text{Si})_2\text{E}$ where E=O, S, Se, Te

IV.1 ^1H AND ^{13}C NUCLEAR MAGNETIC SPECTRA

Over the last two decades nuclear magnetic resonance spectroscopy (n.m.r.) has occupied a leading position among the various spectroscopic methods, and in fact, it now appears to be recognized as an independent scientific discipline. The fundamental feature of the n.m.r. spectra is the appearance of two parameters, the chemical shifts of equivalent nuclei and the spin-spin coupling constants between magnetically non equivalent nuclei. Both parameters, the chemical shift and the coupling constant, are closely associated with the electronic structure of a molecule. The ^1H chemical shifts are dependent on both magnetic and electric fields, and are very sensitive to the nature and spatial orientation of substituents. Similarly, the carbon-13 chemical shifts indicate both the type and structural environment of each carbon atom. Electronegativity, hybridization, and diamagnetic anisotropy effects all affect the carbon-13 chemical shifts just as they do for protons, but in a more complex fashion^{51,52,53}. The chemical shifts of related compounds may be compared in terms of contributions from magnetically anisotropic atoms or bonds, inductive effects, and others as appropriate. The coupling constants are dependent on electric

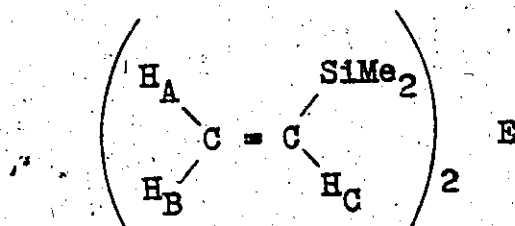
fields , but independent of magnetic fields , and are sensitive to conformation , bond angles , bond lengths , and to the electronegativity of substituents. Both the chemical shift and the coupling constant also depend on external factors such as solvent and temperature.

The usefulness of the chemical shifts and the coupling constants in providing an insight into the electron distribution and bonding characteristics as well as the conformation of molecules is well documented^{54,55}. There has been much concern about the bonding between silicon and electronegative elements or groups. However , the nature of this bonding and , in particular , its variation with the Group IV elements remains a matter for speculation^{54,55}. Quantification of the transmission of substituent effects governing the changes of the n.m.r. parameters presented herein for the new species $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ is , therefore , very difficult.

(a) Description Of The $\text{CH}_2=\text{CH}$ - Proton
Resonance Pattern

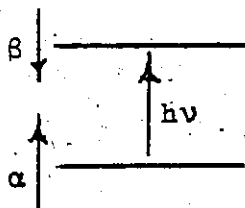
Figures IV.1 - IV.4 at 100.1 MHz and Figures IV.8 and IV.9 at 60 MHz show the ^1H resonance spectra of the four 1,3-divinyl-tetramethyldisilyl chalcogenides , each featuring the resonance pattern characteristic

of the vinyl group. The vinyl group possesses three magnetically non-equivalent hydrogen nuclei, and constitutes a typical ABC spin system. The protons of the vinyl group of the series of compounds may be labeled as follows:

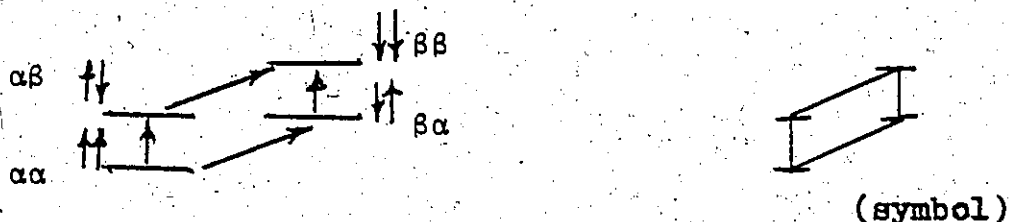


The proton A is trans to C and cis to SiMe_2 , while the proton B is cis to C and trans to SiMe_2 . Thus, A, B, and C all experience different environments and exhibit different chemical shifts. However, the resonance pattern of the $\text{CH}_2=\text{CH}-$ group is not just a chemical shift phenomenon, but arises because of the spin-spin coupling between the three protons.

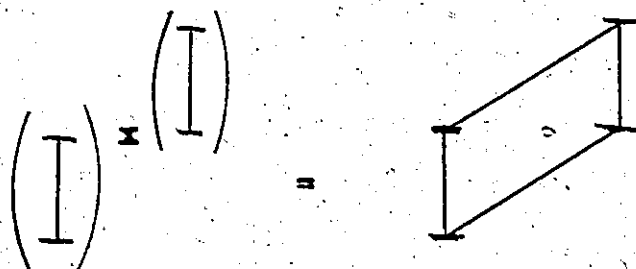
A proposal has been made of analyzing or synthesizing the proton resonance pattern of an ABC three spin system which is approached as follows⁵⁶. First, for one nucleus of spin $1/2$ there are two energy states α and β which can be connected with the corresponding transition, i.e.



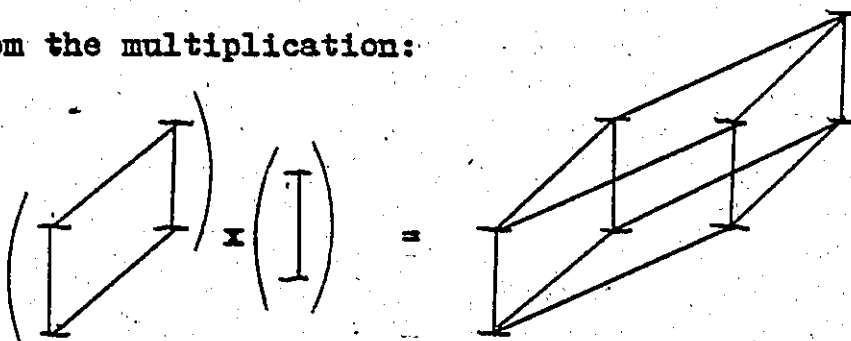
The actual transition may be symbolized with a vertical bar $\overline{}$. Second, for two interacting nuclei with a spin of $1/2$, which constitute an AB case, the energy diagram is as shown below.



An alternate way of looking at this diagram for the two nuclei, is the resultant of the symbolic multiplication:



Thirdly, consider three nuclei with spin of $1/2$, which constitute an ABC case. This system results from the multiplication:



The resultant energy diagram shows that unsymmetrical three-spin system has eight energy levels, and at

high magnetic fields generates 12 strong transitions. The corners of the cube may be taken to represent the eight energy levels, so that when the cube is oriented with one body diagonal vertical, the energy levels are grouped 1,3,3,1 corresponding to states $-3/2$, $-1/2$, $+1/2$, $+3/2$. The three sets of four parallel edges represent the A, B, and C quartets of transition lines. The three body diagonals represent "combination" lines which are indistinguishable from the other 12 lines in some cases. Apparently, in the ^1H n.m.r. spectra of 1,3-divinyl-tetramethyldisilyl chalcogenides, Figures IV.1-IV.4, the 12 resonance lines are clearly observed and determination of the chemical shifts of the three protons and the coupling constants (J_{AC} , J_{AB} , J_{BC}) is a rather involved procedure as compared to other cases, and ideally should be approached by direct computer calculation. However, for the purposes of this study an assignment of the observed frequencies, intensities, and chemical shifts of the $\text{CH}_2=\text{CH}-$ resonance lines was based on comparisons with published vinyl compounds as listed in Table IV.1. The numbering of the resonance lines of the spectra bare a similarity to that of vinyltrimethylsilane, $\text{CH}_2=\text{CHSiMe}_3$ ⁵⁷. The spectra of the vinyl protons of the related silyl species have been analyzed using

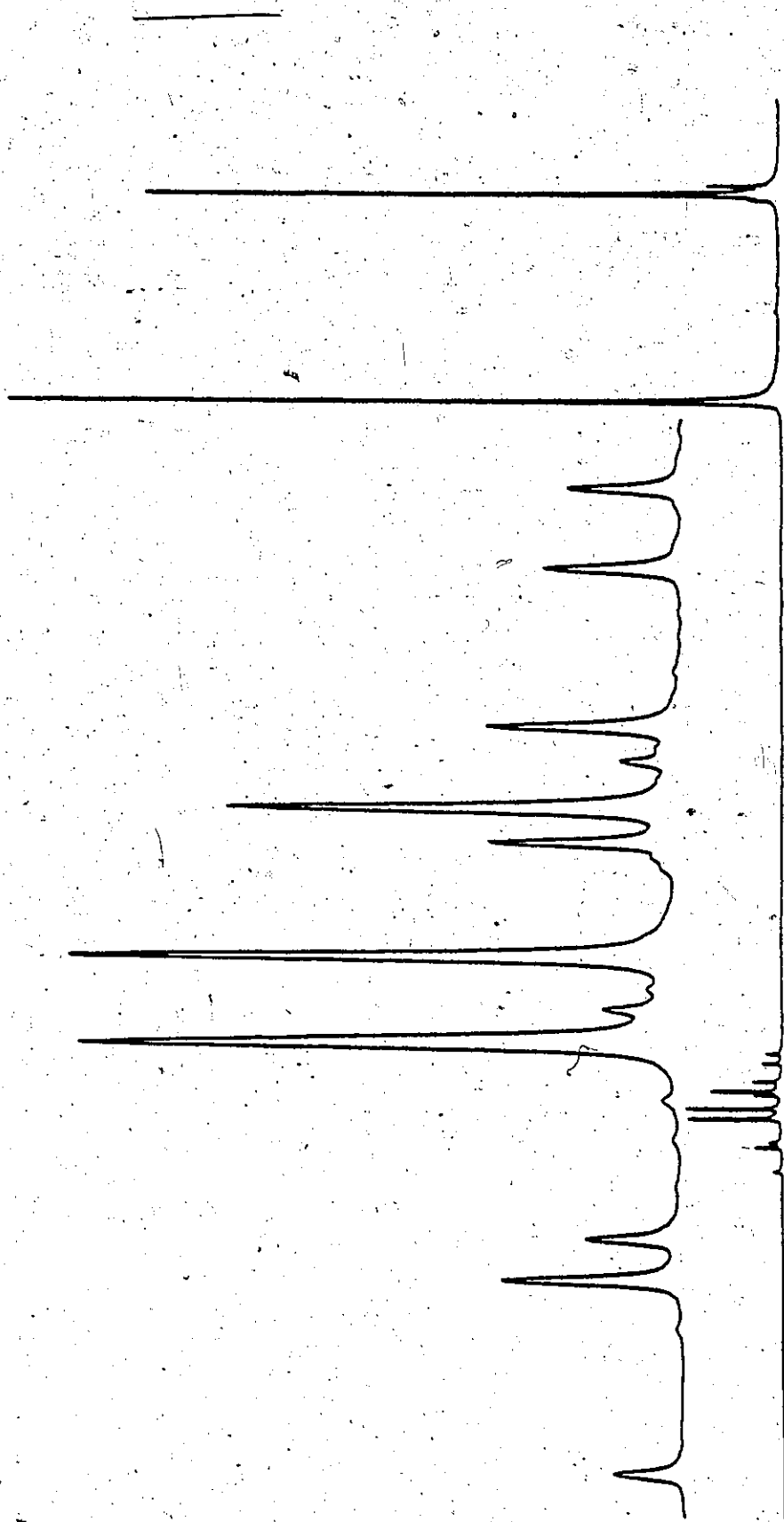


Figure IV.1 The ^1H n.m.r. spectrum of $(\text{VinSiMe}_2)_2\text{O}$ in C_6H_{12} solution at 100.1 MHz.

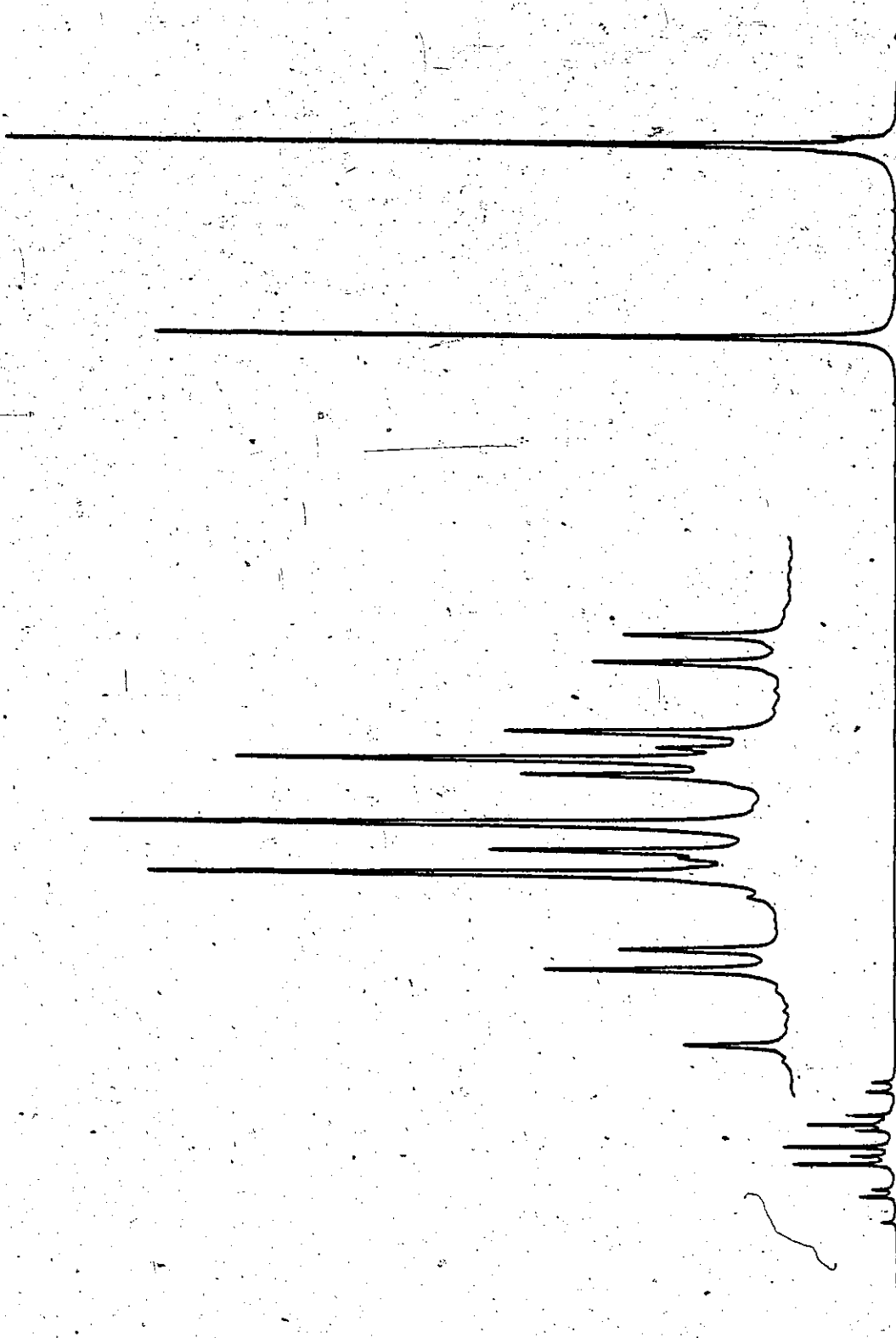


Figure IV.2 The ^1H n.m.r. spectrum of $(\text{VinSiMe}_2)_2\text{S}$ in C_6H_{12} solution at 100.1 MHz.

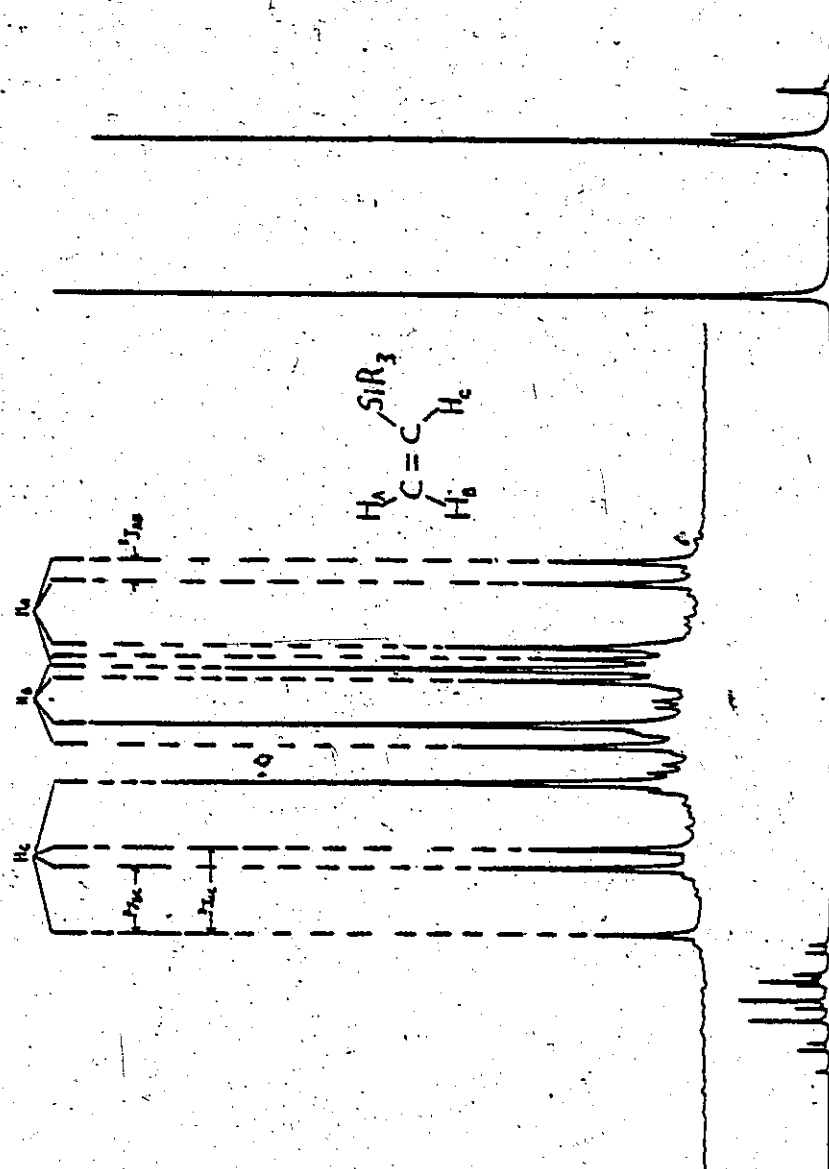


Figure IV.3 The ^1H n.m.r. spectrum of $(\text{VinSiMe}_2)_2\text{Se}$ in C_6H_{12} solution at 100.1 MHz.



Figure IV.4 The ^1H n.m.r. spectrum of neat $(\text{VinSiMe}_2)_2\text{Te}$ at 100.1 MHz.

Table IV.1 The vinyl ^1H n.m.r. parameters of $(\text{VinSiMe}_2)_2\text{E}$ species.*

| LINE | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ | | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{S}$ | | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ | | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Te}$ | | |
|------|---|----------|------|---|----------|------|--|----------|------|--|----------|------|
| | HEIGHT | FREQ(Hz) | PPM | HEIGHT | FREQ(Hz) | PPM | HEIGHT | FREQ(Hz) | PPM | HEIGHT | FREQ(Hz) | PPM |
| 1 | 150.27 | 629.72 | 6.29 | 80.43 | 639.45 | 6.39 | 77.37 | 641.89 | 6.41 | 101.02 | 644.08 | 6.43 |
| 2 | 375.08 | 614.83 | 6.14 | 182.86 | 624.96 | 6.24 | 158.31 | 627.42 | 6.27 | 189.54 | 629.65 | 6.29 |
| 3 | 204.41 | 611.67 | 6.11 | 127.53 | 621.03 | 6.20 | 122.81 | 623.22 | 6.23 | 167.26 | 625.16 | 6.25 |
| 4 | 1206.67 | 596.75 | 5.96 | 472.04 | 606.54 | 6.06 | 379.22 | 608.75 | 6.08 | 410.72 | 610.73 | 6.10 |
| 5 | 168.28 | 594.18 | 5.94 | 222.96 | 602.08 | 6.01 | 176.49 | 600.50 | 6.00 | 224.01 | 595.72 | 5.95 |
| 6 | 1224.37 | 590.09 | 5.90 | 515.60 | 596.86 | 5.96 | 429.46 | 595.72 | 5.95 | 607.82 | 591.35 | 5.91 |
| 7 | 397.54 | 581.41 | 5.81 | 199.87 | 587.57 | 5.87 | 172.43 | 586.02 | 5.85 | 300.46 | 590.21 | 5.89 |
| 8 | 915.09 | 578.79 | 5.78 | 408.70 | 584.59 | 5.84 | 335.08 | 583.52 | 5.83 | 112.50 | 582.63 | 5.82 |
| 9 | 131.90 | 575.21 | 5.75 | 101.16 | 582.39 | 5.82 | 112.77 | 581.23 | 5.80 | 462.59 | 579.85 | 5.79 |
| 10 | 400.96 | 572.59 | 5.71 | 212.78 | 579.40 | 5.79 | 181.19 | 578.74 | 5.78 | 255.34 | 575.60 | 5.75 |
| 11 | 286.45 | 560.75 | 5.60 | 147.73 | 566.18 | 5.66 | 127.51 | 564.86 | 5.64 | 166.03 | 560.90 | 5.60 |
| 12 | 236.89 | 554.55 | 5.54 | 124.68 | 560.99 | 5.60 | 110.81 | 560.07 | 5.60 | 141.51 | 556.69 | 5.56 |

*The spectra were recorded at 100.1 MHz in cyclohexane solution at room temperature. The numbering of the lines is tentative. The frequencies (591.35-582.63 Hz) for the telluride deviate from its accuracy because the sample contained some oxide.

the method of Castellano and Waught⁵⁸ modified by Cavanaugh⁵⁹. Differences in the appearance of the resonance pattern are observed when the spectra recorded at 100.1 MHz (Figures IV.1-IV.4) and 60 MHz (Figures IV.8-IV.9) are compared. However, even at high-field strength (100.1 MHz) significant complicating effects are still present. Closer examination of the spectra (Figures IV.1-IV.4) shows that replacement of S (Se or Te) by the more electronegative oxygen with smaller magnetic anisotropy leads to some collapse of the (ABC) spectrum, such that the lines 4 and 5 appear as a single line. In all cases the proton H_C on the α -carbon experiences the largest deshielding which increases progressively as the chalcogen changes from oxygen to tellurium. The changes in the chemical shift values of the resonance lines involving the protons A and B are small (the chemical shifts relate to individual protons by means of the relation $J_{trans} > J_{cis} > J_{gem}$) between the sulphide, selenide, and telluride. The largest shift along the series can be seen between the oxide and the sulphide.

(b) Methyl Protons And Carbon-13 Chemical Shifts

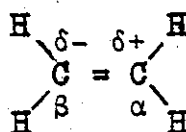
The observed methyl proton and carbon-13 parameters of $(CH_2=CHSiMe_2)_2E$ vs. $(H_{3-n}SiMe_n)_2E$ where

$E=O, S, Se, Te$; and $n=2, 3$ are given in Table IV.2. The 1H and ^{13}C n.m.r. spectra are shown in Figures IV.1-IV.4 and Figures IV.5-IV.6, respectively. The 1H n.m.r. spectra of $(VinSiMe_2)_2E$ show that the methyl resonance is a single peak, indicating the absence of any observable coupling with the vinyl proton (H_c) on the α -carbon. The values of the proton chemical shifts of the methyl group $^1H \delta(Me)$ of $(VinSiMe_2)_2E$ fall generally between the values of those obtained for $(HSiMe_2)_2E$ and $(SiMe_3)_2E^{60}$. The general trend of decreasing of $^1H \delta(Me)$ in the sequence $E=Te \rightarrow Se \rightarrow S \rightarrow O$ persists in the three series of compounds. Similar trends for other Group IV species have been discussed in terms of a major contribution from diamagnetic anisotropy of the substituents and related intramolecular effects⁶¹. Closer examination of $^1H \delta(Me)$ of the vinyl species reveals that the values are essentially the same as those for $(HSiMe_2)_2E$ where $E=O, S, Te$ and $(SiMe_3)_2E$ where $E=S, Se, Te$. Thus, the largest deviation in the magnitude of $^1H \delta(Me)$ is shown between the selenides $[(VinSiMe_2)_2Se(0.45 \text{ p.p.m.}) \text{ and } (HSiMe_2)_2Se(0.51 \text{ p.p.m.})]$ and oxides $[(VinSiMe_2)_2O(0.12 \text{ p.p.m.}) \text{ and } (SiMe_3)_2O(0.06 \text{ p.p.m.})]$ with chemical shift differences of 0.06 p.p.m. While the shift of $^1H \delta(Me)$ values from 0.06 \rightarrow 0.12 \rightarrow 0.14 p.p.m. in the series $(SiMe_3)_2O \longrightarrow$

$\rightarrow(\text{CH}_2=\text{CHSiMe}_2)_2\text{O} \rightarrow (\text{HSiMe}_2)_2\text{O}$ (0.14 p.p.m.) implies weakening of the oxygen silicon ($p \rightarrow d$) π bonding, the magnitude of ^1H $\delta(\text{Me})$ values for the selenides $(\text{SiMe}_3)_2\text{Se}$ 0.42 $\rightarrow (\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ 0.45 $\rightarrow (\text{HSiMe}_2)_2\text{Se}$ 0.51 p.p.m. suggests that the vinyl group behaves as do the methyl, although the electronegativity of the vinyl group has been inferred to be comparable to that of a hydridic hydrogen atom⁶². The effect of the vinyl group is, however, large upon the carbon-13 chemical shifts, such that the trend of shielding parallels only that of $(\text{SiMe}_3)_2\text{E}$. The magnitude of the values indicate that the methyl carbon in the vinyl-containing species are more shielded and the shielding increases as it does for the protons in the series $\text{Te}(3.60) \rightarrow \text{Se}(2.67) \rightarrow \text{S}(2.28) \rightarrow \text{O}(-0.44)$ p.p.m. As can be seen from Figure IV.7, there is, in general, a linear relationship between the ^{13}C and ^1H chemical shifts for $\text{E}=\text{S}, \text{Se},$ and Te . The linear correlation suggests that similar factors are responsible for the observed trends in the ^{13}C and ^1H chemical shifts.

The straightforward assignment of the ^{13}C n.m.r. peaks of the $\text{CH}_2=\text{CH}-$ group was based on the relative intensities of the ^{13}C signals and comparison with the $\delta(^{13}\text{C})$ values for the related species⁶³. As can be

seen from Table IV.2 and Figures IV.5 and IV.6. The carbon-13 resonances of the sp^2 carbons appear considerably down-field relative to those of the sp^3 carbon. The shielding of the sp^3 carbons is much more sensitive to substituent changes than the sp^2 carbons. Thus as the chalcogen changes from oxygen to tellurium there is a slight successive down-field shift in the $^{13}C(sp^2)$ resonances matching a larger similar shift in the sp^3 resonances. The effect of chalcogen change is markedly attenuated upon $\delta^{13}C(sp^2)$ such that the values of $\delta(C_\beta)$ and $\delta(C_\alpha)$ are relatively small between the selenide and telluride ($\Delta=0.02$ p.p.m.), and the sulphide and selenide (0.07 p.p.m.), respectively. In contrast to the successive down-field shift of the $^{13}C(sp^2)$ resonances from oxygen to tellurium, the internal chemical shift $\Delta = \delta(C_\alpha) - \delta(C_\beta)$ increases from Se (7.04) \rightarrow S (7.17) \rightarrow Te (7.21) \rightarrow O (7.98) p.p.m. It has been suggested⁶⁴ that the internal chemical shift is a measure of a double bond polarization in the concept of (a) and if other ef-



(a)

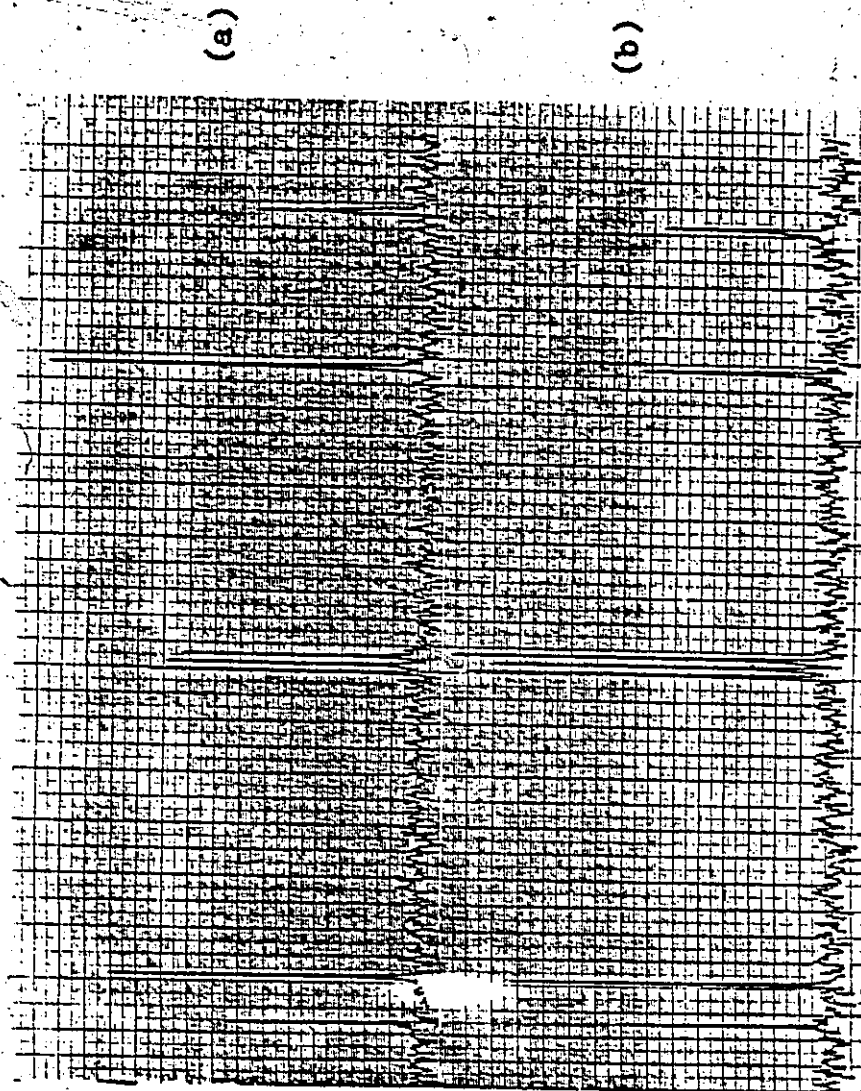


Figure IV.5 The ^{13}O n.m.r. spectra of $(\text{VinSiMe}_2)_2\text{O}$ (a) ;
and $(\text{VinSiMe}_2)_2\text{S}$ (b) in C_6H_{12} solution.

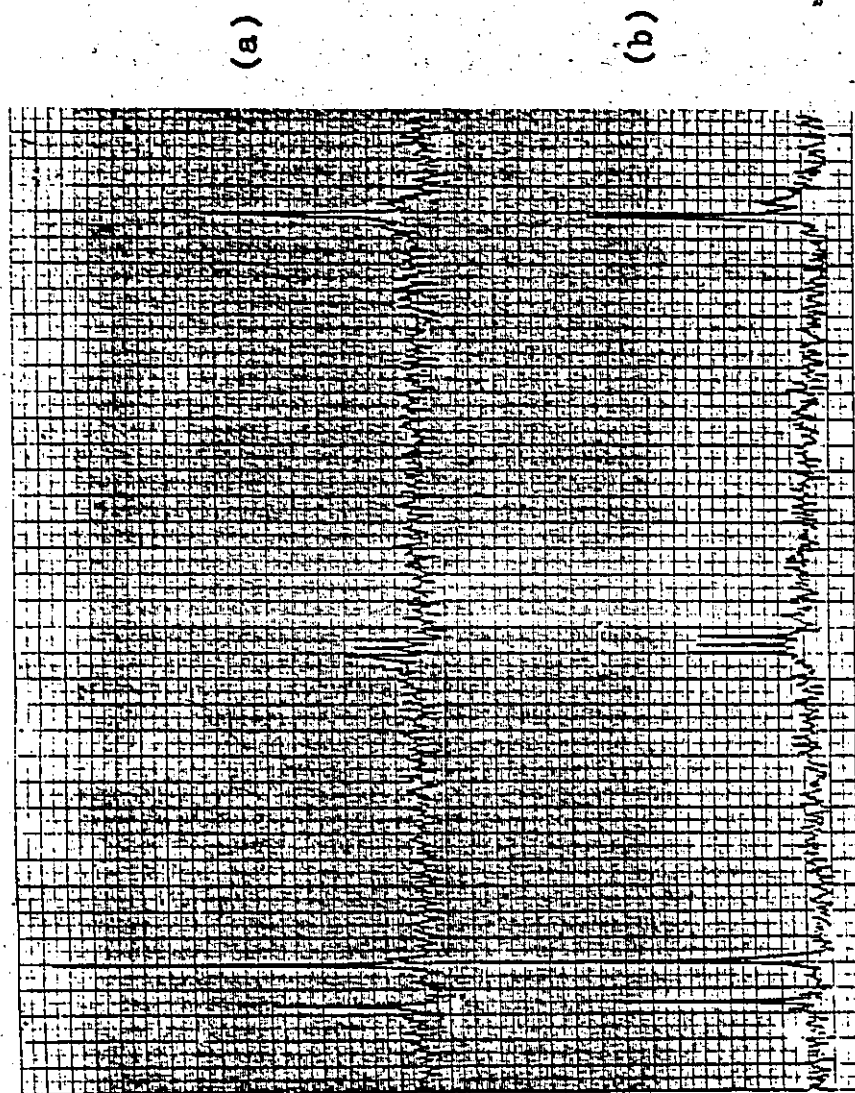


Figure IV.6 The ^{13}C n.m.r. spectra of neat $(\text{VinSiMe}_2)_2\text{Se}$ (a) and $(\text{VinSiMe}_2)_2\text{Te}$ (b).

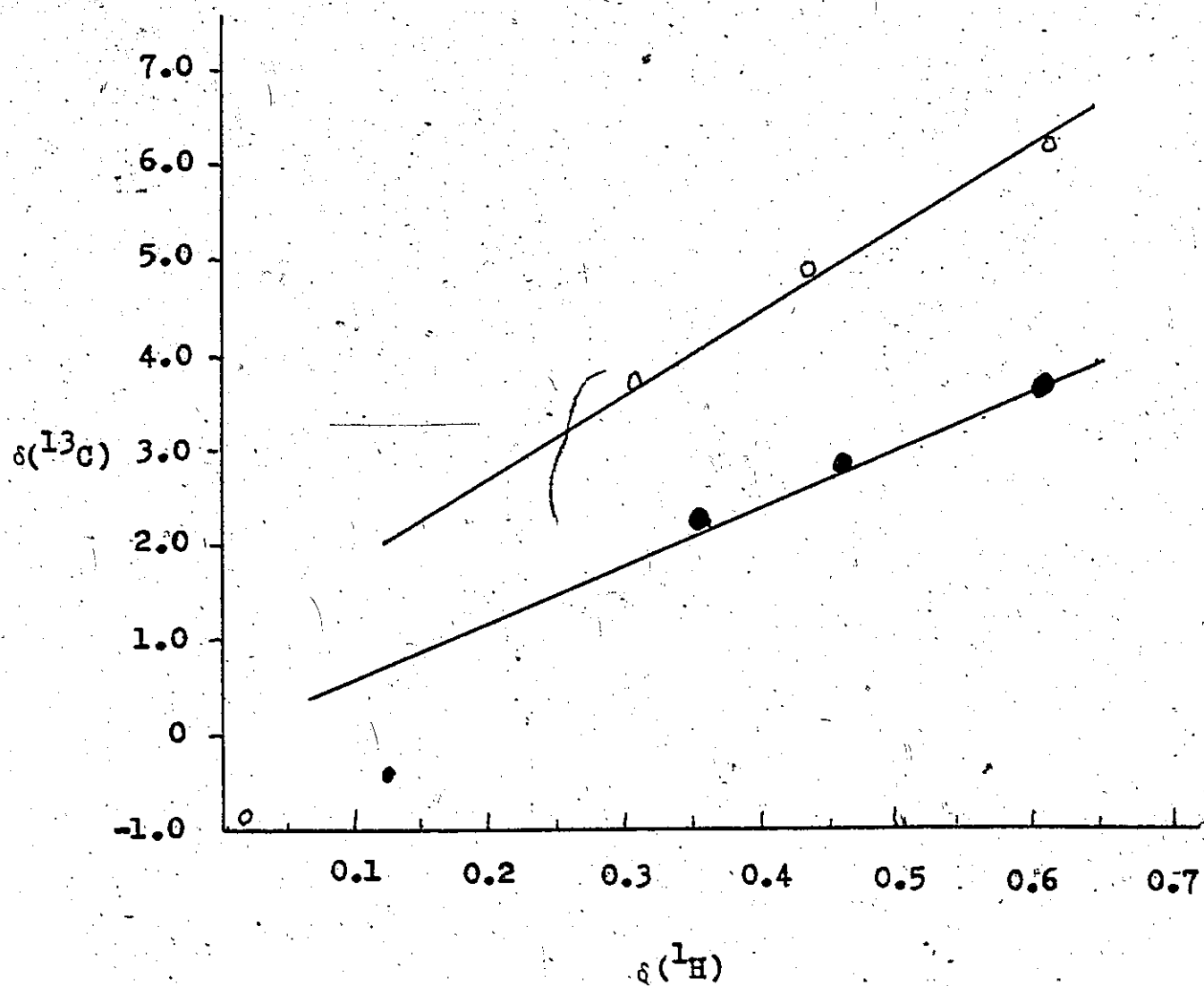


Figure IV.7 ^{13}C chemical shifts as a function of the ^1H chemical shifts (p.p.m.). The points \bullet and \circ refer to $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ and $(\text{SiMe}_3)_2\text{E}$ respectively.

Table IV.2 Changes in chemical shifts and coupling constants
of $(\text{O}(\text{U}_2=\text{CHSiMe}_2)_2\text{E})^+$ vs. $(\text{H}_{3-n}\text{SiMe}_n)_2\text{E}$ species.

| | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ | | | $(\text{HSiMe}_2)_2\text{E}$ vs. $(\text{SiMe}_3)_2\text{E}$ | | |
|----|---|----------------------------------|------------------------------------|--|----------------------------------|----------------------------------|
| | $^1\text{H}\delta(\text{Me})$ | $^{13}\text{C}\delta(\text{Me})$ | $^{13}\text{C}\delta(\text{CH}_2)$ | $^{13}\text{C}\delta(\text{CH})$ | $^{13}\text{C}\delta(\text{Me})$ | $^{13}\text{C}\delta(\text{Me})$ |
| E | | | | | | |
| O | 0.12 | -0.44 | 130.85 | 138.83 | 0.14 | 0.06 + |
| S | 0.36 | 2.28 | 131.92 | 139.09 | 0.38 | 0.31 + |
| Se | 0.45 | 2.67 | 132.12 | 139.16 | 0.51 | 0.42 + |
| Te | 0.60 | 3.58 | 132.14 | 139.35 | 0.63 | 0.58 + |

The spectra were recorded at ambient temperature at 60 and 100,1 MHz*. The values were

partially taken from ref. 8.

fects remain constant, increased polarization should increase the Δ value. Nevertheless, the deshielding or the chemical shift of the C_β is presumably controlled by the π -electron density and that of C_α by δ electron density, though other effects may also contribute.

(c) Coupling Constants

The coupling constants $J(^{13}\text{CH})$ were measured from the well-resolved satellites of the methyl resonances (Figures IV.8 and IV.9). Satellites were also observed that arose from long-range spin-spin coupling involving ^{77}Se and ^{125}Te suggesting that exchange, if any, of silyl groups must be slow.

Earlier investigations of element-hydrogen spin-spin coupling have established that, the coupling constants increase with increasing s-character for the element-hydrogen bond⁶⁵. The s-character of the C-H bond generally depends on the hybridization of the carbon (e.g. sp^3 in CH_3- , sp^2 in $\text{CH}_2=\text{CH}-$, and sp in $\text{CH}\equiv\text{C}-$ group) and the electronegativity of other groups at carbon or neighbouring atoms, which tend to increase the s-character of the C-H bond. The $^{13}\text{C-H}$ coupling constants for the vinyl-containing species are presented in Table IV.2 and exhibits the expected trend. Apparently the trends emerge readily as they

do for the $\delta(\text{Me})$, such that the values fall between those for the system of $(\text{SiMe}_3)_2\text{E}$ and $(\text{HSiMe}_2)_2\text{E}$. Clearly, the effect of the chalcogen is substantial and leads to an increase in the $^{13}\text{C-H}$ coupling constants along the series $\text{O}(118.0) \rightarrow \text{S}(119.6) \rightarrow \text{Se}(120.7) \rightarrow \text{Te}(121.5)$ Hz. This increase implies an increasing electronegativity from oxygen to tellurium which violates chemical sense and suggests that the s-character hypothesis (the Fermi contact term) might not dominate the coupling mechanism between the carbon and hydrogen. Nevertheless, it is interesting to observe that the efficiency of sulphur, selenium, and tellurium in transmitting the effects is greater relative to oxygen. Considering that E (E=S, Se, Te) has electron-accepting d-orbitals and lone-pair electrons available for electron donation, and that silicon also has electron-accepting d-orbitals, it appears possible that the hybrid orbitals in the heavy atom skeleton C-Si-E could be affected. In this way the larger values may reflect the larger fraction of s-character induced by silicon in the C-H bond as the chalcogen changes from oxygen to tellurium. On the other hand, substitution of methyl or vinyl group by hydrogen leads to an increase of the $^{13}\text{C-H}$ coupling constants indicating that both methyl and vinyl groups

are behaving as less electronegative groups than hydrogen. Whether this dependence of the $^{13}\text{C-H}$ coupling is a result of changes in the s-character of the orbitals involved, or due to angular distortion, or bond shortening is a matter of controversy.

The proton-proton coupling constants $J(\text{HH})$ for the vinyl group are given in Table IV.3. The assignment (Figure IV.3) and the determination are only tentative, and disclose the changes of the values as the chalcogen changes. While the coupling between the protons A and C ($^3J_{\text{AC}}$) increases as the chalcogen changes from oxygen to tellurium, as does $J(^{13}\text{CH})$, the coupling between the protons A and B ($^3J_{\text{AB}}$) and between B and C ($^2J_{\text{BC}}$) decreases as does the sum of the three coupling constants $[\Sigma J = 39.11 (\text{O}) \longrightarrow 38.10 (\text{S}) \longrightarrow 37.93 (\text{Se}) \longrightarrow 37.64 (\text{Te})]$. Evidently, the magnitude of ΣJ follows the effective electronegativity of the chalcogen (E) and it would be highly speculative to make further discussion, since the factors governing the magnitude of the coupling constants cannot be said to be fully understood and must be complex.

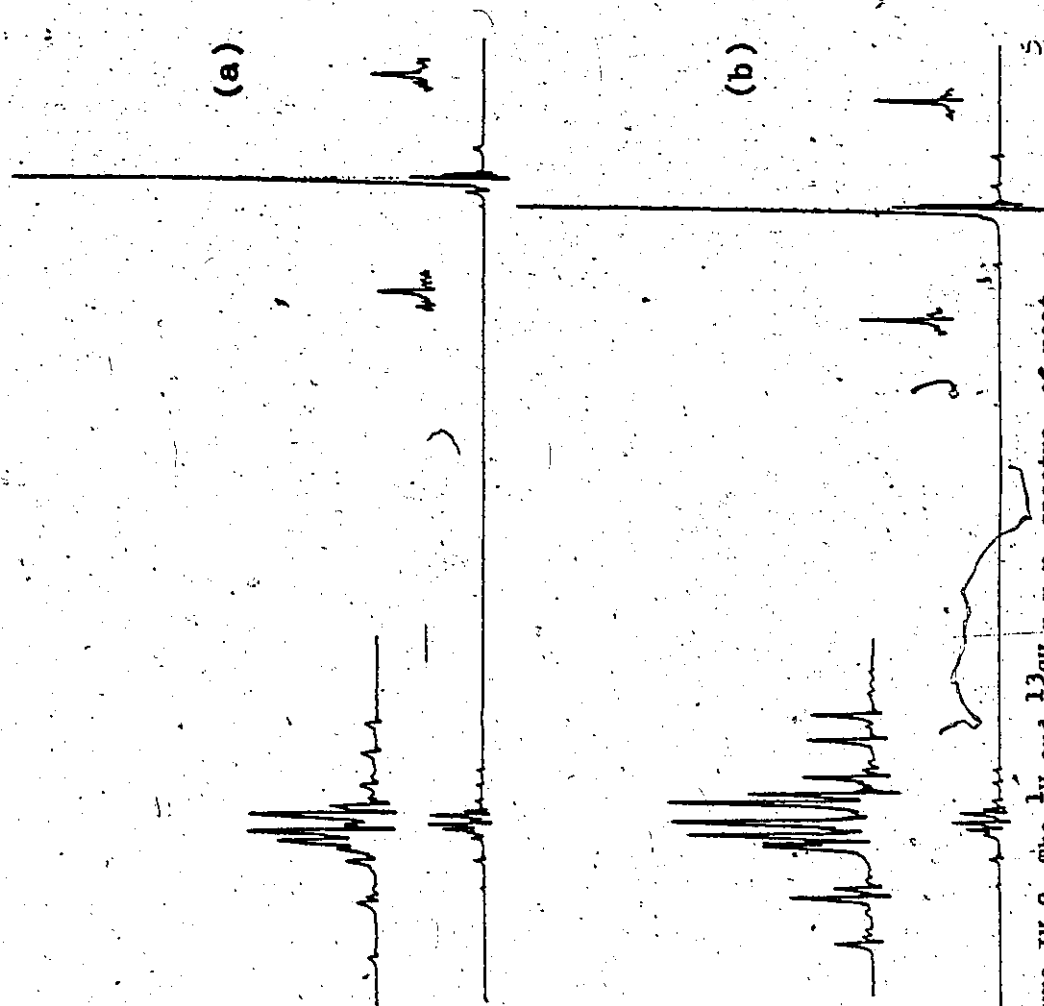


Figure IV.8 The ^1H and ^{13}CH n.m.r. spectra of neat $(\text{VinSiMe}_2)_2\text{O}$ (a); and $(\text{VinSiMe}_2)_2\text{S}$ (b).

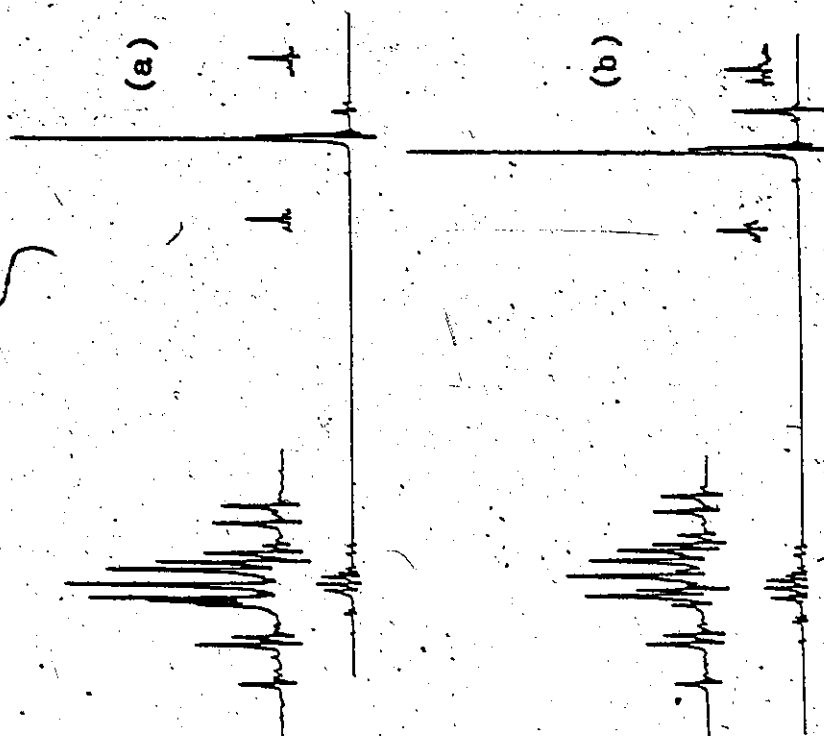
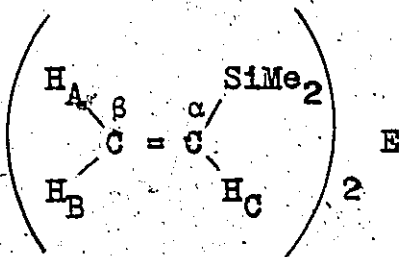


Figure IV.9 The ^1H and ^{13}CH n.m.r. spectra of neat $(\text{VinSiMe}_2)_2\text{Se}$ (a); $(\text{VinSiMe}_2)_2\text{Te}$ (b).

Table IV.3 The coupling constants of the vinyl protons*. The spectra were recorded at 100.1 MHz in cyclohexane solution. The assignment and the magnitude of the coupling constants are tentative, see Figure IV.3.

| E | $^3J_{AC}$ | $^3J_{BC}$ | $^2J_{AB}$ | ΣJ |
|----|------------|------------|------------|------------|
| O | 18.03 | 14.89 | 6.19 | 39.11 |
| S | 18.42 | 14.49 | 5.19 | 38.10 |
| Se | 18.67 | 14.47 | 4.79 | 37.93 |
| Te | 18.92 | 14.43 | 4.29 | 37.64 |

* The corresponding coupling constants in $\text{CH}_2=\text{CHSi}(\text{CH}_3)_3$ are $^3J_{AC} = 20.4$, $^3J_{BC} = 14.6$, and $^2J_{AB} = 3.8$ with $\Sigma J = 38.8$, see reference 57.



IV.2 VIBRATIONAL SPECTRA

Vibrational spectroscopy is an important tool for the characterization of various species. Valuable information regarding molecular structures, intra- and intermolecular forces as well as molecular force constants can be extracted from vibrational spectral data. Many studies have been done on the vibrational spectra of vinyl derivatives of Group IV elements^{18,61,66-68}. Conflicting conclusions have been reached not only over the assignment of the vibrations of the vinyl group, but also on the extent of a vinyl-metalloid and metalloid-chalcogen π -interaction. The observed frequencies and intensities, changes of $\nu(\text{C}=\text{C})$ and the vibrations of the $\text{CH}_2=$ group have been taken as a measure of the vinyl-metalloid π -interaction⁶¹. Similarly, the observed $\nu(\text{M}-\text{C})$ frequency changes for compounds of the formula $(\text{Et}_3\text{M})_n\text{E}$ ($\text{M}=\text{Si}, \text{Ge}$; E =element in Group I-VII; n =valence of E) have been interpreted in terms of the capacity of E for $(p-d)\pi$ bonding with M . It has been concluded that the $\nu(\text{M}-\text{C})$ frequencies are linearly related to the electronegativity of E ⁶¹. In the following discussion the i.r. and Raman spectra of 1,3-divinyl-tetramethyldisilyl chalcogenides; $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$, where $\text{E}=\text{O}, \text{S}, \text{Se}, \text{Te}$ are examined consecutively. Representative spectra are presented

in Figures IV.10-13. The observed frequencies and tentative assignments of the vibrational modes are summarized in Table IV.4. The vibrational assignments were made by comparison along the series $O \rightarrow S \rightarrow Se \rightarrow Te$ and with those of $(CH_2=CHSiMe_2)_2O^{43}$, $CH_2=CHSiMe_2Cl^{18}$, $(CH_2=CH)_4Si^{68}$, $(CH_2=CH)_3B^{69}$ and $(CH_2=CH)_3P^{70}$.

Features associated with CH stretches are expected to be at highest wavenumbers, and the three Raman bands are seen at $\nu_a(CH_2)$ ca. 3053, $\nu(CH)$ ca. 3008 and $\nu_s(CH_2)$ ca. 2969 cm^{-1} with corresponding i.r. absorptions of weak to strong intensities. Except for the oxide, the $\nu_s(CH_2)$ stretching frequency is indistinguishable from the $\nu_a(CH_3)$ mode. The $\nu_s(CH_3)$ mode is observed as a very strong polarized band at ca. 2902 cm^{-1} with a weak i.r. counterpart. The CH_2 scissors vibration is expected to give a band at about 1404 cm^{-1} where the $\delta_a(CH_3)$ vibration appears. Similarly, the $\delta(CH)$ is obscured by the $\nu(Si-O)$ mode at 510 cm^{-1} . The $\delta(CH_2)$ is assigned at somewhat higher frequency at ca. 1440 cm^{-1} as a very weak absorption. The remaining vibrations appearing at: $\rho(CH)$ ca. 1264, $\delta_{tw}(CH)$ ca. 1000, $\delta_{vag}(CH_2)$ ca. 947 and $\delta_s(CH_3)$ ca. 1242 cm^{-1} are unambiguously assigned. This assignment is in agreement with previous

Figure IV.10 The liquid phase infrared spectra of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ (a);
and $(\text{CH}_2=\text{CHSiMe}_2)_2\text{S}$ (b).

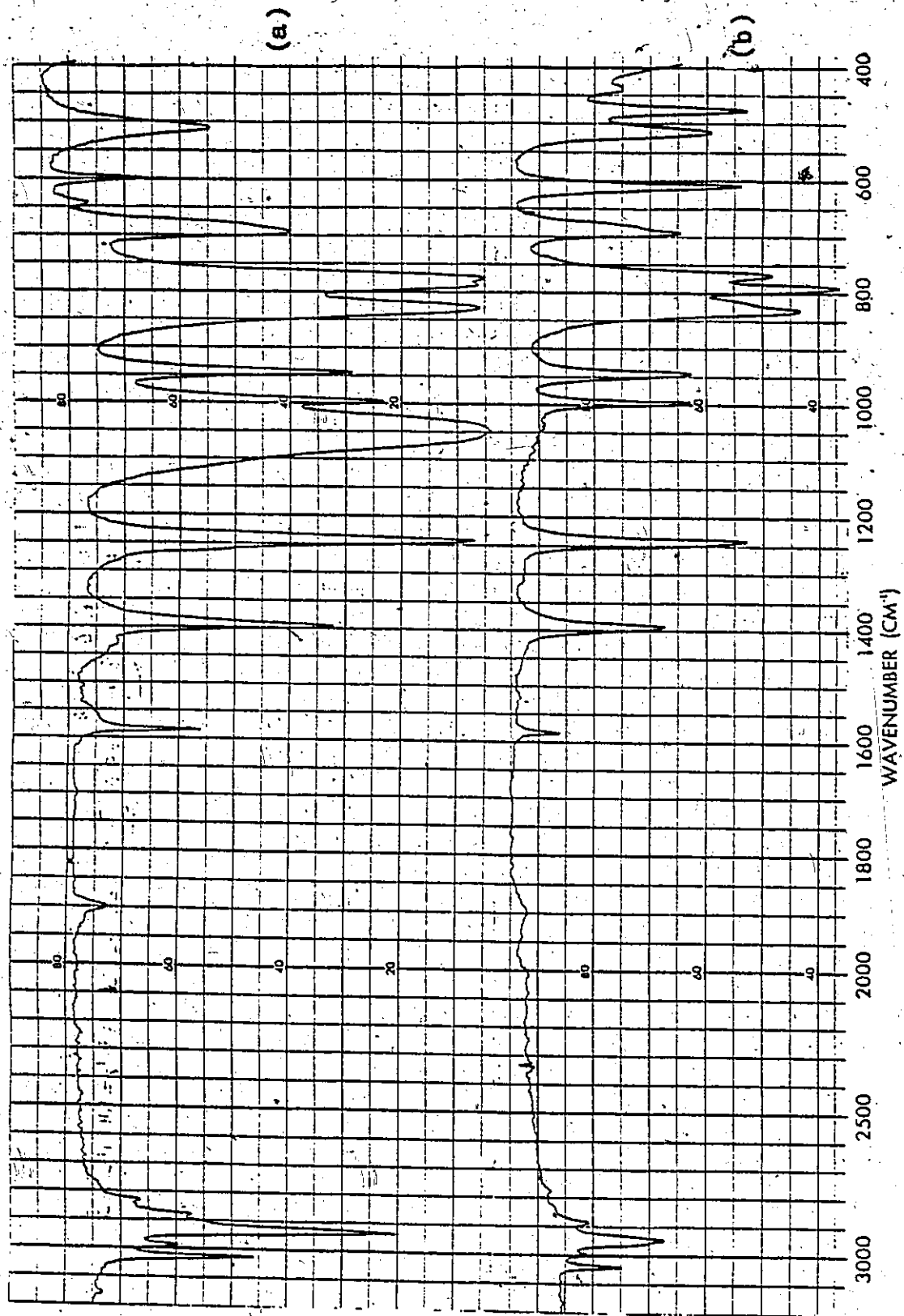


Figure IV.11 The liquid phase infrared spectra of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ (a);
and $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Te}$ (b).

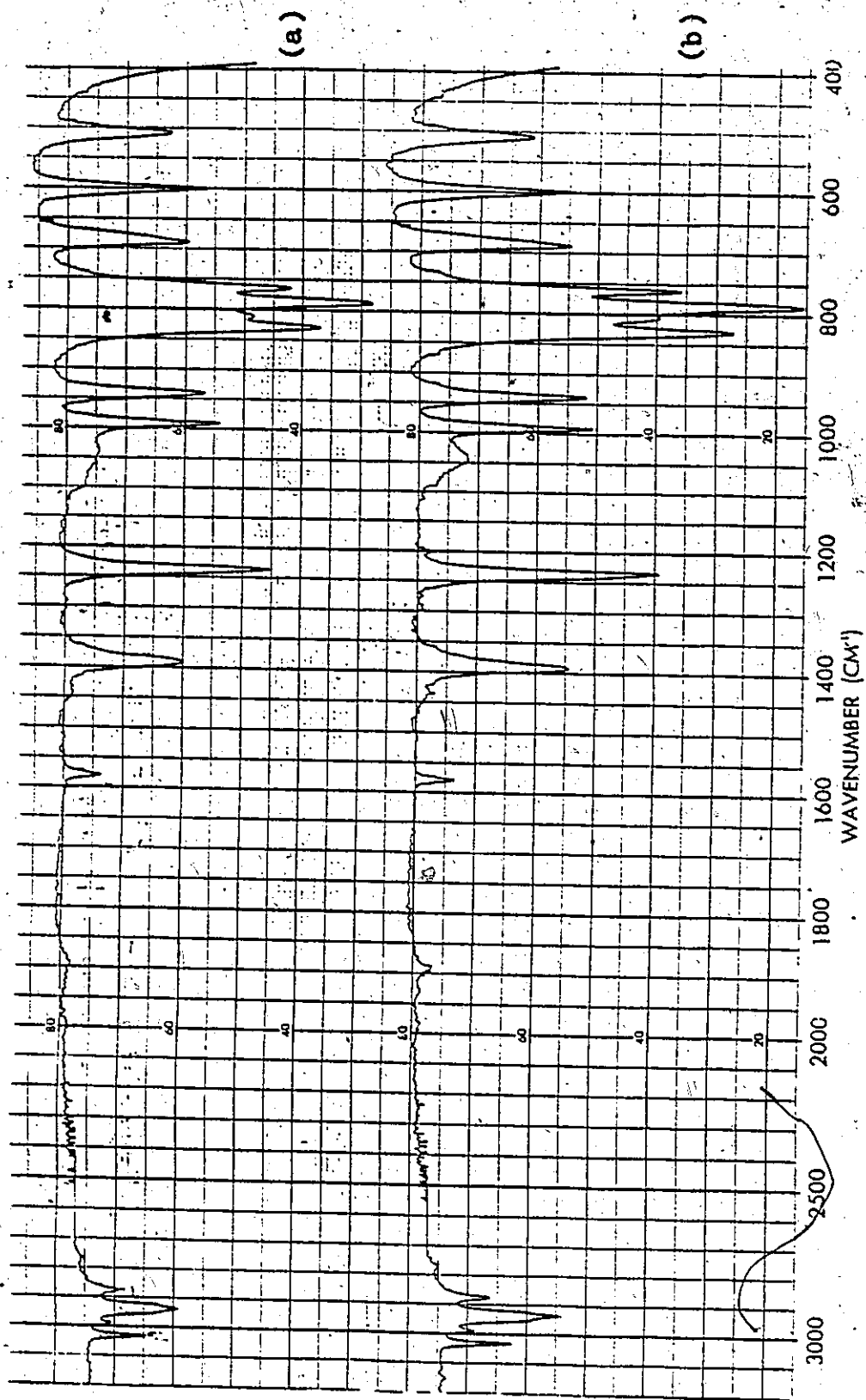


Figure IV.12 The liquid phase Raman spectrum of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$.

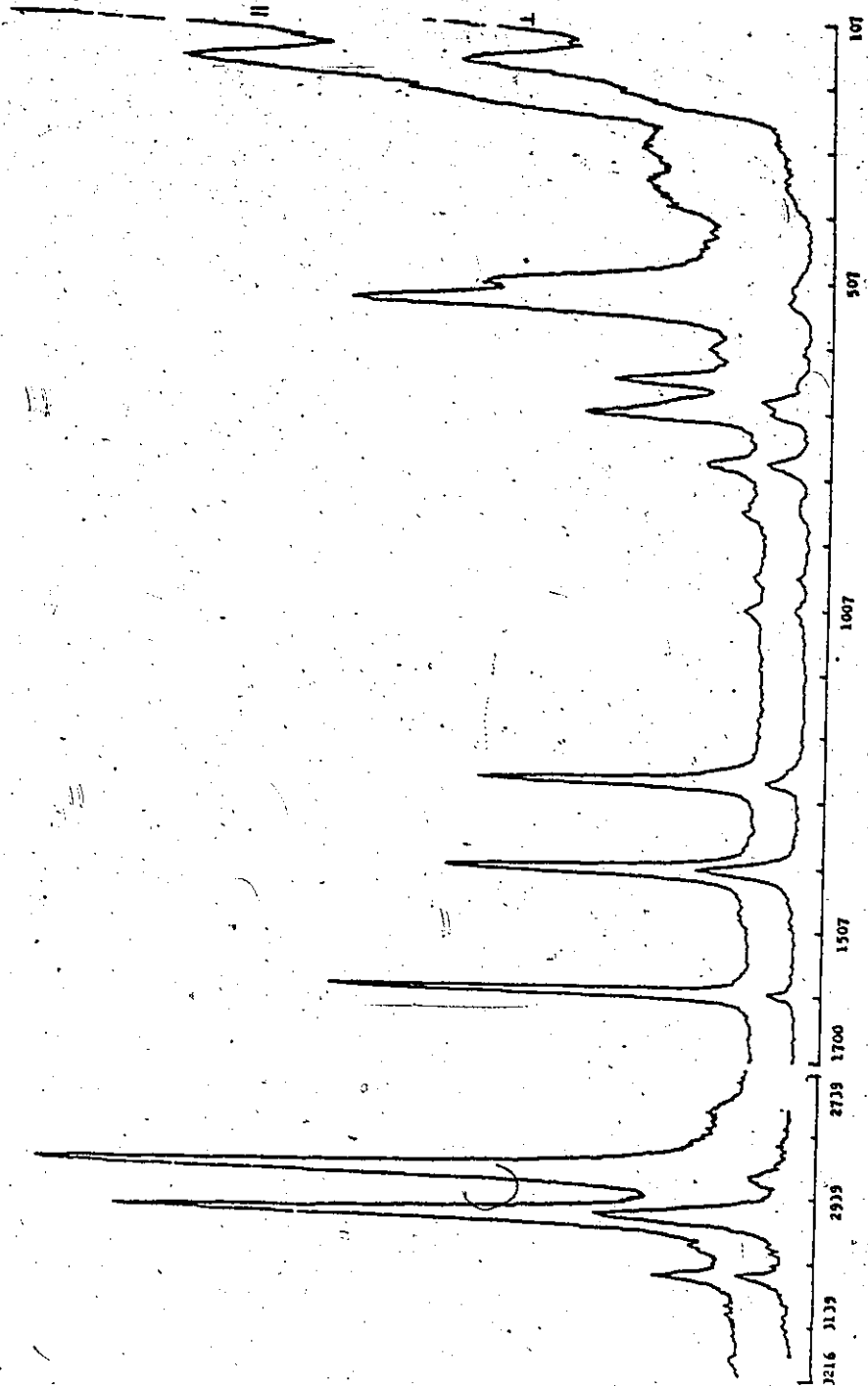


Figure IV.13 The liquid phase Raman spectrum of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$.

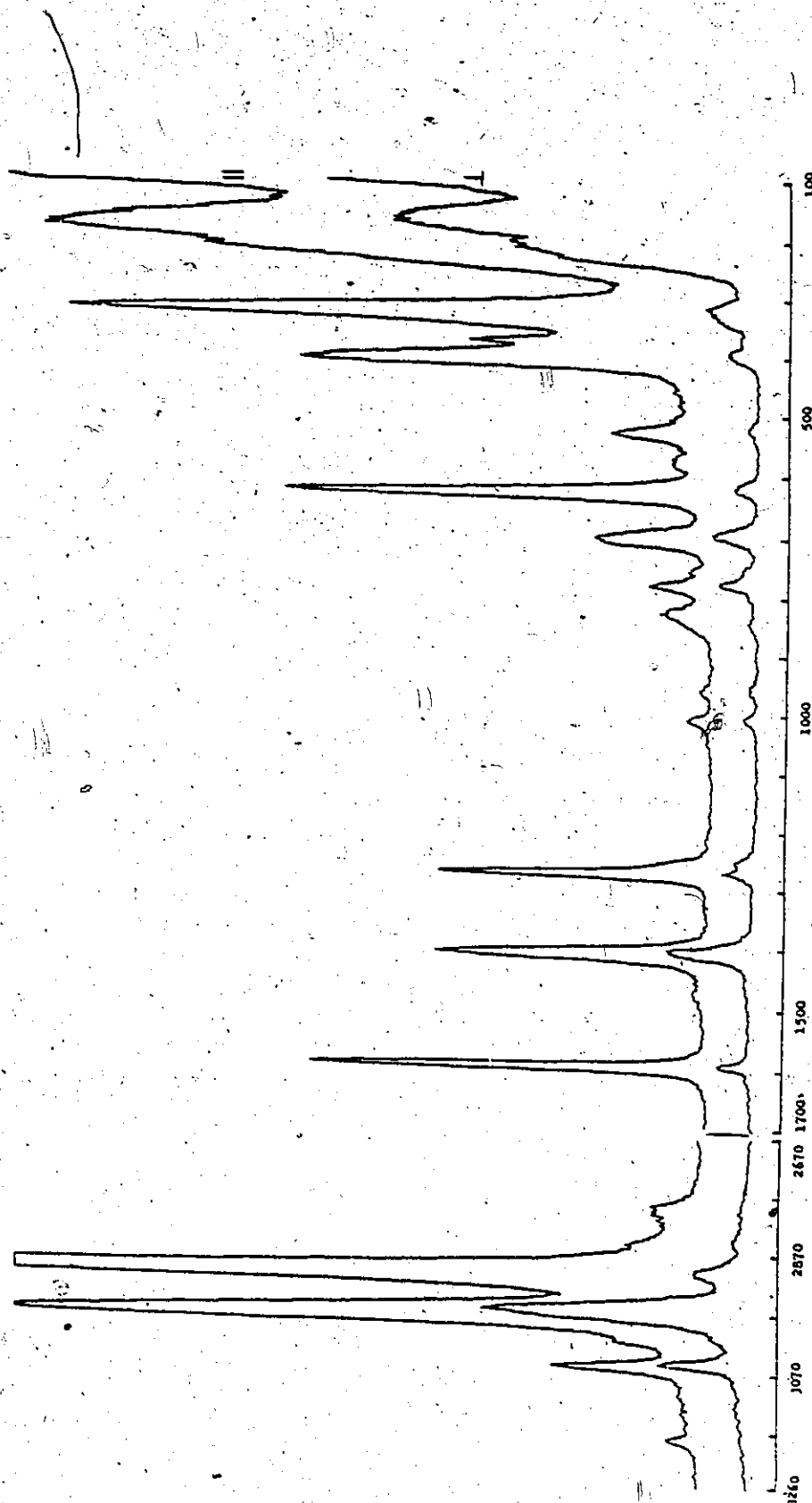


Table IV.4 The i.r. and Raman spectra (cm^{-1}) of the bis(vinylidimethylsilyl) chalcogenides.*

| Tentative Assignment | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{S}$ | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ | | $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Te}$ | |
|--|---|--------------|---|--------------|--|--------------|--|--------------|
| | i.r. | Raman | i.r. | Raman | i.r. | Raman | i.r. | Raman |
| $\nu(\text{CH}_2=)$ | 3045m | 3054mdp | 3040m | 3051mdp | 3031m | 3055mdp | 3033m | 3053mdp |
| $\nu(-\text{CH}-)$ | 3005w | 3013wshp | 2998w | 3008wsh | 2990w | 3008wshp | 2988w | 3005wshp |
| $\nu(\text{CH}_3), (\text{CH}_2=)$ | 2951s | 2969vshp | 2948m | 2967vshp | 2939m | 2972vshp | 2936m | 2968vshp |
| $\nu(\text{CH}_3)$ | 2891wsh | 2902vshp | 2888w | 2898vshp | 2878 | 2902vshp | 2875 | 2896vshp |
| $\nu(\text{O}=\text{O})$ | 1585m | 1596sp | 1585m | 1589sp | 1580m | 1594vshp | 1580m | 1589sp |
| $\nu(\text{CH}_2=)$ | 1440brsh | ca. 1469vshp | ca. 1478vshp | ca. 1478vshp | 1435vw | ca. 1471vshp | 1435vw | ca. 1469vshp |
| $\nu(\text{CH}_3), \nu_{\text{sc}}(\text{CH}_2)$ | 1397s | 1408msp | 1393s | 1404msp | 1391s | 1405sp | 1391s | 1405msp |
| $\rho(-\text{CH}-)$ | 1260wsh | 1273msp | 1241vs | 1269msp | 1246vs | 1269sp | 1245vs | 1269msp |
| $\nu(\text{CH}_3)$ | 1242vs | 1253vshp | 1241vs | 1247wshdp | 1246vs | 1248wshdp | 1245vs | ca. 1247vshp |
| $\nu_{\text{as}}(-\text{CH}-)$ | 997s | 1008mdp | 996s | 1005vshdp | 992s | 1006mdp | 992s | 1003vw |
| $\nu_{\text{as}}(\text{CH}_2=)$ | 947s | 955vshdp | 945s | 954vshdp | 940s | 957vshdp | 940s | ca. 940vshp |
| $\rho(\text{CH}_3)$ | 830vs | 854vshdp | 832vs | 830vshdp | 830vs | 825sp | 830vs | 818wp |
| | 787vs | 783mdp | 791vs | 778mdp | 788vs | 780mdp | 788vs | 777mdp |
| $\nu_{\text{as}}(\text{SiO})$ | 775vs | | 769s | 754w | 764s | 755wsh | 762s | ca. 754vshp |
| | 693ms | 706mp | 692ms | 702mp | 690ms | 701mp | 690ms | 697wp |
| $\nu_{\text{as}}(\text{SiO})$ | 680wsh | 686mdp | 680wsh | ca. 686mdp | 680wsh | | | |
| | 643w | 656mp | | 632sp | | 627sp | 645vshp | 620mp |
| $\rho(-\text{CH}-)$ | 600m | 608wp | 610ms | ca. 601vshp | 600ms | ca. 581vw | 600ms | 574wp |
| | 510ms | 512shp | 515m | 530mp | 509m | 528mp | 510m | 525msp |
| $\nu(\text{Si-E})$ | 510ms | | 478ms | 487sh | 390ms | | | |
| | 391w | 542vshp | 441w | 448vshp | | 398sp | | 297vshp |
| | 367vw | 388wshp | | 390vw | ca. 365wsh | 370wp | | 378mp |
| skeletal def. | 315wbr | 358wshp | | 345mp | ca. 340wbr | | | 325sh |
| | ca. 210wbr | 316wshp | | ca. 319vshp | ca. 315wbr | 313vshp | ca. 306 | |
| | | 210wsh | | 224sh | 205vw | 202wsh | | 192sp |
| | | 172mdp | | 169mdp | | 170mdp | | 165sh |
| | | | | | | ca. 73vshp | | |

* Spectra recorded at R.T.

Abbreviations used: v, very; b, broad; sh, shoulder; s, strong; m, medium; ms, moderately strong; w, weak; p, polarized; dp, depolarized.

+ Coincident with (Si-O).

reports presented elsewhere^{18,43,68,69,70}.

The stretching vibration attributed to the presence of the C=C bond in the molecules has a wave-number of about 1592 cm^{-1} in the Raman effect with a corresponding i.r. counterpart. The stretching vibrations arising from the C_3Si skeleton contribute to a number of features between ca. 787 and ca. 574 cm^{-1} . These have been assigned by analogy with previous assignments in the literature for vinyl^{18,43,68} and related compounds⁵⁰. As the Si-E-Si bond stretching vibrations are the most characteristic of the new chalcogenides their positions fall at 1049 vs and $542\text{ sp}(\theta)$; $448\text{ vsp}(\text{S})$; $398\text{ vsp}(\text{Se})$; and $297\text{ cm}^{-1}(\text{Te})$. The lowering of $\nu(\text{Si-E})$ arises because of the increased mass of the chalcogen, and may also reflect weakening of the Si-E bond. Similar trends of decreasing Si-E stretching frequencies have been observed in the stretching frequencies occurring in related silyl species⁵⁰, $(\text{Me}_n\text{H}_{3-n}\text{Si})_2\text{E}$. The remaining vibrational degrees of freedom involve only the deformations of the C=C-Si-E-Si-C=C skeletal frame and they appear in the low-frequency region. The frequency of the Si-E-Si deformations decrease, as expected, less rapidly than the frequency of the skeletal stretching. The resulting trend of decreasing deformation frequencies for Si-E-Si along the series

confirmed that the heavy atom skeletons are bent at the central atom as are the related species.

The force constants of the Si-E bonds were calculated by making the naïve assumption that in the 1,3-divinyl-tetramethyldisilyl chalcogenides the Si-E bond can be treated as a diatomic molecule, the average values of the Si-E asymmetric and symmetric stretches were taken as the stretching vibrations of the assumed diatomics. The Si-E (E=O,S,Se,Te) bond force constants so calculated give the values listed in Table IV.5. Despite the fact of the exaggerated approximation, the values of the force constants disclose the expected trend where the force constant of Si-O is very much greater than the other Si-chalcogen bonds, which suggests a much greater rigidity of the Si-O bond compared to the remaining Si-chalcogen bonds. This, is of course in keeping with the general stability of compounds containing Si-O bonds where a degree of Si-O π -bonding has been invoked. Given the gross approximation, the calculated values still suggest a bond of similar rigidity in the case of Si-S and Si-Se but a weaker bond for Si-Te. This is consistent with the observation that tellurium metal was usually deposited during the course of recording an i.r. spectrum.

(a) Force constant calculations

$$\Delta\epsilon = h/2\pi \sqrt{k/\mu} \quad \text{thus} \quad k = 4\pi^2 \mu \Delta\epsilon^2 / h^2$$

$$\Delta\epsilon = h\nu \quad \bar{\nu} = 1/\lambda \quad \nu = c/\lambda \quad \nu = c\bar{\nu}$$

therefore $\Delta\epsilon = hc\bar{\nu}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N}$$

where $\Delta\epsilon$ = The energy of a quantum of radiation in erg.

h = Planck's constant 6.62×10^{-27} erg-sec.

μ = The reduced mass of a diatomic molecule.

c = Velocity of light 3.00×10^{10} cm/sec.

N = Avogadro's number 6.023×10^{23} .

λ = The wavelength of radiation.

ν = Frequency in cycles per second.

$\bar{\nu}$ = The wave number in reciprocal centimeters.

m_1 and m_2 = The atomic mass of atom one and the atomic mass of atom two in a diatomic molecule.

k = The force constant of the bond of a diatomic molecule.

Atomic mass of silicon = 28.086

" " oxygen = 15.999

Average of $\bar{\nu}$ (i.r.) and $\bar{\nu}$ (Raman) of Oxygen

$$\begin{aligned}\bar{\nu} &= 1049 + 542 / 2 \\ &= \underline{796} \text{ cm}^{-1} \text{ for oxygen}\end{aligned}$$

$$\begin{aligned}\Delta\epsilon &= 6.62 \times 10^{-27} \times 3.00 \times 10^{10} \times 796 \\ &= 15808.56 \times 10^{-17} \\ &= \underline{1.58 \times 10^{-13}} \text{ erg}\end{aligned}$$

$$\begin{aligned}\mu &= \frac{28.09 \times 16.00}{28.09 + 16.00} \times \frac{1}{6.02 \times 10^{23}} \\ &= \frac{449.44}{265.42} \times 10^{-23} \\ &= \underline{1.69 \times 10^{-23}} \text{ gm}\end{aligned}$$

$$\begin{aligned}K &= \frac{4(3.14)^2 \times 1.69 \times 10^{-23} \times (1.58 \times 10^{-13})^2}{(6.62 \times 10^{-27})^2} \\ &= \frac{166.32}{43.82} \times 10^5 \\ &= \underline{3.8 \times 10^5} \text{ dyne/cm}\end{aligned}$$

The force constant of the remaining Si-E (E=S, Se, Te) bonds were calculated in an analogous manner.

Table IV.5 The force constants of the Si-E (E=O,S,Se,Te) bonds*.

| <u>FORCE CONSTANTS</u> | | | |
|--|--------------------------------|------------------------|----------------------------|
| $\bar{\nu}$ Average of ν_a and ν_s <u>cm⁻¹</u> | $\Delta\epsilon$ <u>erg</u> | μ <u>gm</u> | κ <u>dyne/cm</u> |
| 796 | 1.58×10^{-13} | 1.69×10^{-23} | 3.8×10^5 |
| 463 | 9.20×10^{-14} | 2.48×10^{-23} | 1.9×10^5 |
| 394 | 7.82×10^{-14} | 3.44×10^{-23} | 1.9×10^5 |
| 297 | 5.90×10^{-14} | 3.82×10^{-23} | 1.2×10^5 |

*The trend of the force constants⁷² of Si-halide bonds (Si-F 5.3×10^5 ; Si-Cl 2.3×10^5 ; and Si-Br 1.8×10^5 dyne/cm) is similar to those of Si-chalcogen bonds.

IV.3 THE MASS SPECTRUM OF $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$

The field ionization and electron impact mass spectra of 1,3-divinyl-tetramethyldisiloxane were recorded with the aim of molecular weight confirmation and structural elucidation. The mass spectra of the heavier analogues were not recorded because of their extreme sensitivity to hydrolysis. The molecular ion, $(\text{C}_8\text{H}_{18}\text{Si}_2\text{O})^+$ was present in both spectra but of very low abundance m/e 186, <1.0%. The most abundant ion is that formed by the elimination of a methyl group, $\text{M}^+ - \text{CH}_3$ m/e 171 (100%). Further analysis of the electron impact spectrum disclosed that the fragmentation pattern is very similar to that published by Tamas et al.⁷³, thus the fragmentation will not be discussed here.

IV.4 THE REACTIVITY OF 1,3-DIVINYLTETRAMETHYLDISILYL CHALCOGENIDES

The reactions of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ with some simple species including anhydrous HX ($\text{X}=\text{Cl}, \text{Br}$), aqueous HCN , SO_2F_2 , CCl_3SCl , CH_3SH , H_2S and H_2Se are described. The reactions were carried out in sealed tubes at various temperatures and the identification of the products was achieved by ^1H n.m.r. spectroscopy.

IV.5 EXPERIMENTAL

(a) Reaction of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{E}$ with anhydrous HX (X=Cl, Br)

The reaction of the Si-E bond where E=S, Se, Te with HX is described in chapter III.2(d), p. 28. The analogous reaction of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ (0.0289 g, 0.1554 mmol) was carried out with an excess of anhydrous HCl (0.700 mmol) and trace amounts of cyclohexane. Initial observation of the ^1H n.m.r. spectrum revealed proton resonances of only the starting material $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$, ^1H $\delta(\text{Me})$ 0.12 p.p.m. After longer reaction times, weak proton resonances attributable to $\text{CH}_2=\text{CHSiMe}_2\text{Cl}$ were observed at ^1H $\delta(\text{Me})$ 0.43 p.p.m.

(b) Reaction of $(\text{VinSiMe}_2)_2\text{O}$ with aqueous HCN

Hydrogen cyanide was prepared by the addition of aqueous solution of NaCN onto H_2SO_4 containing some FeSO_4 . The reaction is exothermic and HCN was collected in a storage vessel as it was formed. Excess of hydrogen cyanide containing some moisture was sealed with $(\text{VinSiMe}_2)_2\text{O}$ (0.0412 g, 0.2215 mmol) and traces of TMS. When the tube was shaken immiscible droplets were formed. The ^1H n.m.r. spectrum disclosed resonances of only the starting materials:

(VinSiMe₂)₂O ¹H δ(Me) 0.13 p.p.m.; δ(HCN) 2.62 p.p.m. and δ(H₂O) 4.10 p.p.m. The tube was placed in an oven set at 120° and after three days there was no change in the ¹H n.m.r. spectrum.

(c) Reaction of (CH₂=CHSiMe₂)₂O with SO₂F₂

In a typical run 0.3670 mmol of (CH₂=CHSiMe₂)₂O was sealed with an excess of SO₂F₂ (0.900 mmol) and trace amounts of TMS. The ¹H n.m.r. spectrum showed the resonances of only the oxide.

(d) Reaction of (CH₂=CHSiMe₂)₂O with CCl₃SCl

Typically, (CH₂=CHSiMe₂)₂O (0.4023 mmol) and CCl₃SCl (0.8132 mmol) with trace amounts of TMS were sealed into a semimicro n.m.r. tube. After 16 hours the ¹H n.m.r. spectrum was recorded and revealed the proton resonances of only the oxide.

(e) Reaction of (CH₂=CHSiMe₂)₂O with CH₃SH

Typically, (VinSiMe₂)₂O (0.0138 g, 0.0742 mmol) and methane thiol, CH₃SH, (0.1637 mmol) were sealed with trace amounts of TMS in a semimicro n.m.r. tube. The ¹H n.m.r. spectrum of the reaction at R.T. disclosed the resonances of only the starting materials. The sealed tube was then placed in an oven at 120°. After 24 hours there was a definite change of the colour from colourless to

yellow. The proton n.m.r spectrum revealed additional weak resonances at 2.70 , 2.33 and 0.31 p.p.m. indicating a slight addition of CH_3SH to the vinyl group with the formation of $(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SiMe}_2)_2\text{O}$.

(f) Reaction of $(\text{VinSiMe}_2)_2\text{S}$ with H_2S

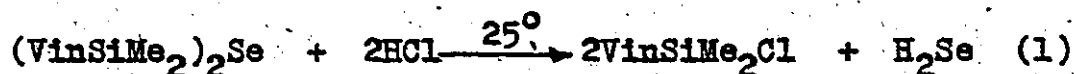
The sulphide , $(\text{VinSiMe}_2)_2\text{S}$ (0.0306 g , 0.1515 mmol) and an excess of anhydrous H_2S (0.500 mmol) were sealed in a semimicro n.m.r. tube with some TMS. The ^1H n.m.r. spectrum of the reaction was recorded after 10 minutes and disclosed only the resonances of the starting materials $(\text{VinSiMe}_2)_2\text{S}$ ^1H $\delta(\text{Me})$ 0.38 and $\delta(\text{H}_2\text{S})$ 0.82 p.p.m. After longer reaction time (ca. 14 days) there was essentially no change in the reaction.

(g) Reaction of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ with H_2Se

Typically , $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ (0.0831 g , 0.3382 mmol) and an excess of H_2Se (1.1230 mmol) were sealed in a semimicro n.m.r. tube. The ^1H n.m.r. spectrum of the reaction was recorded after 16 hours and revealed resonances centred at ca. 2.68 , ca. 1.50 , ca. 1.29 , ca. 0.48 , ca. -0.83 and a very weak peak at ca. -2.82 p.p.m. assignable to $(\text{HSeCH}_2\text{CH}_2\text{SiMe}_2)_2\text{Se}$ and presumably traces of $\text{HSeCH}_2\text{CH}_2\text{SiMe}_2\text{SeH}$, Figure IV.14.

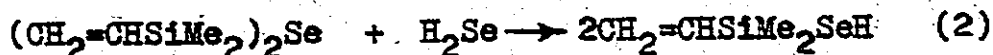
IV.6 DISCUSSION

The Si-E (E=S, Se, Te) bond is generally less stable than the Si-O bond, this trend was also seen in the force constants of the Si-E bonds. As mentioned earlier, compounds containing the Si-E bonds are almost all unstable to air and moisture. Their thermal stability generally decreases with increasing atomic weight of E. As an extension of previous work⁵⁰, the cleavage of the Si-E-Si linkage with anhydrous HX (X=Cl, Br) was conducted for observation of reactivity and structural confirmation. Aside from the siloxane linkage Si-O-Si, these bonds are readily cleaved by HX followed by the formation of $\text{CH}_2=\text{CHSiMe}_2\text{X}$ and the respective H_2E , i.e.,

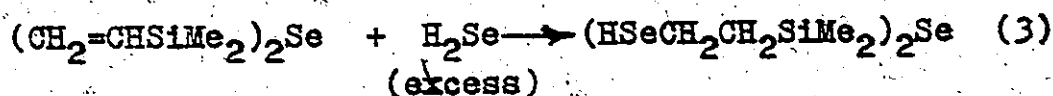


Earlier studies have shown that the M-E-M (M=Si, Ge) skeleton in the related species $(\text{Me}_n\text{H}_{3-n}\text{M})_2\text{E}$ reacts with the corresponding H_2E with the formation of chalcogenols $\text{Me}_n\text{H}_{3-n}\text{M}-\text{EH}$ ^{49,50}. In this study these reactions were attempted not only from the point of view of chemical reactivity of the metalloid-chalcogen bond, but also because they might provide

synthetic pathways to some new vinyl containing silyl species, such as $\text{CH}_2=\text{CHSiMe}_2\text{SeH}$, according to reaction (2). However, this reaction was

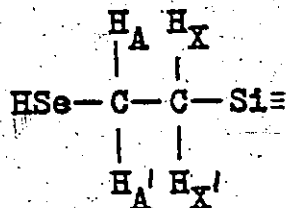


not observed but rather there was evidence that H_2Se underwent addition across the double bond according to reaction (3). Thus, in a sealed tube reaction, the selenide reacted with an excess of hydrogen selenide to yield $(\text{HSeCH}_2\text{CH}_2\text{SiMe}_2)_2\text{Se}$ i.e.



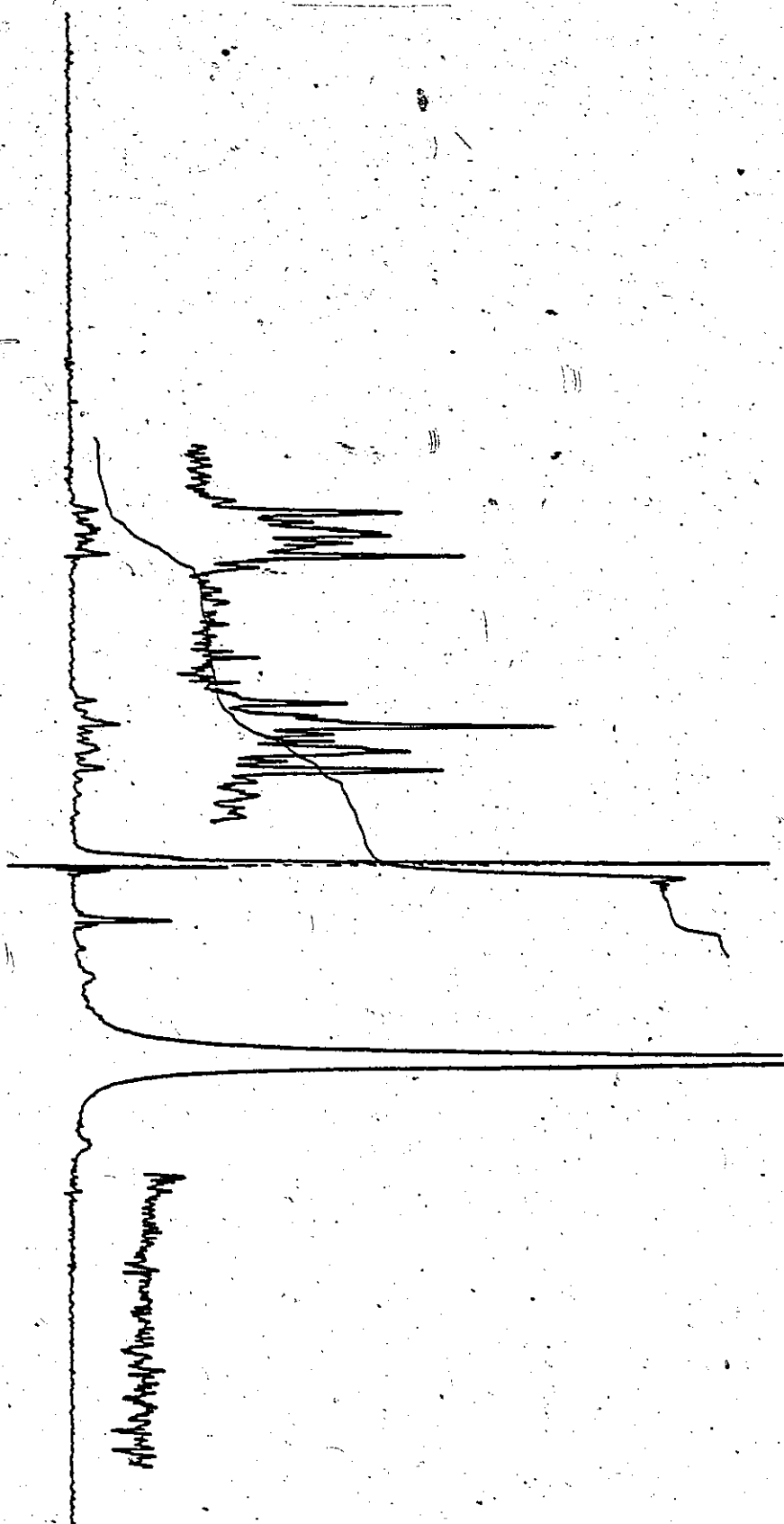
The reaction was followed by sequential recording of the ^1H n.m.r. spectrum. The observed ^1H n.m.r. spectrum of reaction (3) is presented in Figure IV.14. An examination of the spectrum reveals that the reaction of $(\text{CH}_2=\text{CHSiMe}_2)_2\text{Se}$ with H_2Se yields $(\text{HSeCH}_2\text{CH}_2\text{SiMe}_2)_2\text{Se}$ with anti-Markownikoff orientation (see chapter III, p. 22). The methylene protons of the $-\text{SeCH}_2\text{CH}_2$ fragment form a spin system of $\text{AA}'\text{XX}'$ type. The corresponding chemical shifts were determined from the centre of each of the multi-

plets , i.e. (SeCH_2) ca. 2.68 and (CH_2Si)



ca. 1.29 p.p.m.; and that of (HSe) at ca. 1.50 and (SiMe_2) at 0.48 p.p.m. The values of the proton resonances were determined with respect to the peak appearing at ca. 0.12 p.p.m. assignable to $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$. The appearance of this peak is due to the highly sensitive nature of the Si-Se bond to hydrolysis. The analogous reaction of the sulphide , $(\text{CH}_2=\text{CHSiMe}_2)_2\text{S}$, with hydrogen sulphide did not disclose the addition of H_2S_2 to the vinyl group or cleavage of the Si-S-Si linkage. Similarly , the oxide , $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$, with weakly acidic species such as HCN and MeSH did not react at R.T. These reactions demonstrate the resistance of the Si-E-Si linkage to chemical attack with increasing electronegativity of the chalcogen atom.

Figure IV.14 The ¹H n.m.r. spectrum of (CH=CHSiMe₃)₂Se with H₂Se (excess).



CHAPTER V

PARTIAL HALOGENATION OF SOME

SILANES AND GERMANES

V.1 INTRODUCTION

In this chapter emphasis is placed on the partial halogenation of some silanes and germanes of the general formula $\text{Me}_n\text{H}_{4-n}\text{M}$ where $\text{M}=\text{Si}, \text{Ge}$; $n=0 \rightarrow 3$ and $\text{Me}_3\text{SiSiMe}_3$. The halides $\text{Me}_n\text{H}_{3-n}\text{MX}$ ($\text{X}=\text{halogen}$) are the most important synthetic intermediates with respect to their conversion to other silyl and germyl species. Most of the synthetic routes leading to halogenosilanes and -germanes are well documented. Nevertheless, the initial interest in the preparation of the halogenosilanes and -germanes stemmed from the growing spectroscopic interest involving both X-ray and u.v. photoelectron spectroscopy of these species.⁷⁴⁻⁷⁹ The subsequent concern was directed towards their use in the synthesis of some new silyl and germyl Group VI compounds.

V.2 EXPERIMENTAL

(a) Synthesis Of Iodosilane^{80,82-85} $\text{Me}_n\text{H}_{3-n}\text{SiI}$

A flask containing aluminium triiodide (catalytic amount) was attached to the vacuum line and evacuated while being immersed in a -78° slush bath. Glass wool was placed above the vessel in order to minimize contamination of the vacuum line by iodine. After evacuation the -78° slush bath was replaced by one at -196° , whereupon silane (4.2 mmol) and hydrogen iodide (6.0 mmol)

were condensed into the reaction vessel. After closing the stopcock the contents of the vessel were allowed to warm to -45° , and allowed to react at this temperature for about four hours, at which time the reaction products were allowed to distill through a series of 'U'-traps at -78° , -95° , and -196° with pumping. The fraction at -78° contained traces of SiH_2I_2 . The fraction at -95° contained pure iodosilane, identified by its ^1H n.m.r.²⁸ and vibrational⁸¹ spectra. The fraction at -196° contained unreacted silane and hydrogen iodide. The yield of iodosilane was 70%.

Diiodosilane and triiodosilane were prepared in an analogous manner as iodosilane. Silane (6 mmol) and hydrogen iodide (12 mmol) were reacted in the presence of catalytic amount of AlI_3 . The reaction was allowed to react at R.T. for about 36 hours, whereupon the reaction products were fractionally distilled through traps held in series at -45° , -95° , and -196° . The -196° trap contained unreacted HI , the -95° trap contained no product, and the -45° trap retained the reaction product, the contents of the latter trap was separated into a top and bottom fraction. ^1H n.m.r.²⁸ analysis indicated the presence of H_2SiI_2 (93%) and HSiI_3 (7%) in the top fraction, while the bottom fraction was composed of H_2SiI_2 (82%) and HSiI_3 (18%).

Both the top and bottom fractions were allowed to distil through traps held at -23° and -78° , the latter trap retained diiodosilane, while triiodosilane was condensed into the former trap.

Trimethylsilane was prepared by the reduction⁸⁶ of Me_3SiCl with $\text{Li}[\text{AlH}_4]$ in $n\text{-Bu}_2\text{O}$, it was then utilized as a starting material for obtaining trimethyl-iodosilane, prepared in an analogous manner as above.

(b) Attempted Preparation of $\text{Me}_3\text{SiSiMe}_2\text{Cl}$

The recognition of pentamethylchlorodisilane as an important starting material in many reactions, prompted the attempt to prepare it through the following two reactions:



Reaction⁸⁸ (1) was conducted with a reaction vessel (ca. 100 ml) equipped with a finger, a Teflon-in-glass stopcock, and a ball joint. After charging the reaction vessel with SbCl_5 (4.11 mmol) it was degassed at -78° , whereupon the vessel was cooled to -196° and dichloromethane was condensed into it, followed by hexamethyldisilane (4.47 mmol). The reaction proceeded immediately when the reactants were brought to R.T. The reaction products were passed through traps held in

series at -45° , -78° , and -196° . The solvent condensed in the latter trap, while the products were collected in the -78° trap. The ^1H n.m.r. spectra of the product revealed the presence of Me_3SiCl ¹¹ and Me_2SiCl_2 .⁸⁹

Reaction⁹⁰ (2) was conducted with a reaction vessel (ca. 100 ml) equipped with a finger, a magnetic stirrer, a ball joint, and a stopcock. The vessel was charged with H_2SO_4 (1.56 g) and NH_4Cl (0.23 g) into the finger. The system was attached to the vacuum line, and thoroughly evacuated after being cooled to -78° . The -78° bath was replaced by a -196° bath, whereupon hexamethyldisilane (3 mmol) was condensed into the reaction vessel. Upon warming the reaction mixture to R.T., effervescence was immediately observed. The reaction mixture was stirred at R.T. for about two hours. Thereafter the reaction vessel was immersed in an ice bath, and within a period of 30 minutes NH_4Cl was added dropwise into the reaction mixture by swinging the side arm (finger). The reactants were stirred at R.T. for an additional half hour, whereupon the products were fractionally distilled through traps held at -45° and -196° . Both traps retained reaction products. The contents in the -196° trap were fractionated again through traps held at -78° and -196° , methane (3.5 mmol) was retained in the latter trap as measured by the

manometer. The -78° trap⁹¹ also retained the reaction product. From the ^1H n.m.r. spectra⁹¹ of the products, it was concluded that pentamethylchlorodisilane was not formed, but rather a mixture of products. Possibly chlorinated silanes and -disilanes.

(c) The Preparation of H_3GeCl and H_2GeCl_2

The primary purpose of carrying out the following reaction was to obtain dichlorogermane in high yield, and in addition, using H_2GeCl_2 as a start-



ing material, in order to prepare the remaining dihalogermanes for the purpose of obtaining X-ray photoelectron spectra.

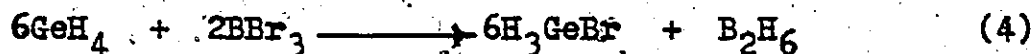
In the preparation^{92,93} of monochlorogermane and dichlorogermane, a reaction vessel (ca. 250 ml) was thoroughly evacuated on the vacuum line, at which time germane (6 mmol) was condensed in the vessel at a temperature of -196° , the reaction vessel was closed and the manifold was thoroughly evacuated, whereupon BCl_3 (4 mmol) was condensed in the above vessel. The reaction mixture was subsequently warmed to -78° and kept at this temperature for 5-6 hours. After this time the reaction products were fractionally distilled through traps held in

series at -78° , -126° , and -196° , nothing was observed in the -78° trap, diborane was retained in the -196° trap, which was removed by condensing it over a large excess of triethylamine⁹². The contents of the -126° trap were redistilled through traps held at -78° and -95° . The products were retained in the latter trap. The ^1H n.m.r. spectra⁹³ indicated that the major product was H_3GeCl , and H_2GeCl_2 was present only in trace amounts.

With the purpose of increasing the yield of H_2GeCl_2 , the reaction time was increased to 24 hours, the reaction temperature was increased to R.T., and an excess of BCl_3 was used. All changes failed to increase the yield of dichlorogermane. Furthermore, reacting H_3GeCl with additional amounts of BCl_3 also failed to increase the yield of H_2GeCl_2 .

(d) The Preparation of H_3GeBr

Bromogermane was prepared⁹² according to reaction (4). A reaction vessel (ca. 250 ml) equipped



with a cold finger and a ball-joint was attached to the vacuum line and thoroughly evacuated, whereupon the vessel was cooled to a temperature of -196° , and BBr_3 (1 mmol) was condensed into the reaction

vessel, followed by germane (3.5 mmol). The reactants were warmed to -78° , and the mixture was allowed to react for about 2 hours. After this time, the volatile products were distilled through traps held in series at -45° , -95° , and -196° . The contents of the -95° trap were redistilled through traps at -63° , -95° , and -196° . The -95° trap retained pure monobromogermane which was identified by its i.r. spectrum⁹⁴, and its purity further confirmed by ^1H n.m.r.¹⁷ The -196° trap retained diborane and some unreacted germane which were discarded.

(e) The Preparation⁹⁵ of Me_3GeF and Me_2GeF_2

A reaction vessel (ca. 50 ml) equipped with a greaseless Teflon-in-glass stopcock, and containing PbO/SbF_3 1:1 (8 g) was thoroughly evacuated on the vacuum line, and Me_3GeBr (3 mmol) was condensed into the above vessel at -196° . The mixture was allowed to react at R.T. for 45 minutes with occasional shaking. After this time the volatile products were distilled through traps held at -23° and -78° . Me_3GeF was retained in the latter trap. Its purity and identity were confirmed by ^1H n.m.r.⁹⁵ spectroscopy.

Difluorodimethylgermane was prepared by passing Me_2GeBr_2 (2 mmol) through a column (45 cm long,

2.5 cm o.d.) loosely packed with a mixture of glass wool and PbF_2 . A pure sample of Me_2GeF_2 was obtained after passing the Me_2GeBr_2 back and forth about twenty times. The identity and purity of Me_2GeF_2 was confirmed by its i.r.⁹⁶ and ^1H n.m.r.⁹⁶ spectra.

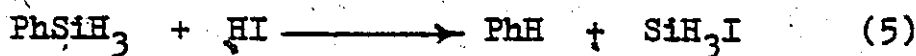
V.3 DISCUSSION

The reactions leading to halogenosilanes and -germanes may be differentiated into those based on the reactivity of silicon and germanium hydrides, and those based on the reactivity of the M-Y bond, where M=Si, Ge; Y= halogen, C, O etc. The parent hydrides SiH_4 and GeH_4 are often used because of their availability, although the tetrahalides have a wide synthetic application. Partially methylated hydrides, $\text{Me}_n\text{H}_{3-n}\text{M}$ where M= Si, Ge; n= 1,2,3 are commonly prepared in high yields by the reduction of the corresponding chloride with LiAlH_4 ($\text{Me}_n\text{MCl}_{3-n}$) in n-butyl ether^{97,98}.

Methylgermane MeGeH_3 is conveniently prepared by deprotonation of germane with KOH in 1,2-dimethoxyethane with subsequent methylation of the intermediate germyl potassium with MeI at low temperature (-10°)⁹⁹.

In general, selective iodination of silanes

$\text{Me}_n\text{H}_{4-n}\text{Si}$ is achieved when they are reacted with a slight deficiency of hydrogen iodide in the presence of catalytic amounts of AlI_3 ^{82-85,80}. Since the Si-H bonds are affected selectively, this type of interaction enables one to carry out further halogenation leading to SiH_2I_2 . Silanes containing Si-aryl bonds can be readily halogenated since such bonds are easily ruptured by anhydrous hydrogen halides, as exemplified by reaction (5). While the cleavage of Si-aryl bonds



is facile, the halogenation of hexamethyldisilane by SbCl_5 or by NH_4Cl and H_2SO_4 proceeds with splitting of the Si-C and Si-Si bonds, hence evoking less interest for the preparation of pentamethylchlorodisilane.

Unlike the silanes, the related iodination of germane with iodine proceeds with good yields of iodogermane, and is accompanied by the formation of HI ²⁶. Iodogermane may also be obtained by halogen exchange reactions either from the chloride or bromide¹⁰⁰.

Chloro- or bromogermane are conveniently prepared^{92,93} by reacting germane with BX_3 (where X=

Cl, Br) at low temperature. However, when further chlorination was attempted only the monochlorogermane was recovered, with small amounts of dichlorogermane. Nevertheless the chlorination of germane with boron trichloride leading to monochlorogermane is facile and clean, while the bromination is somewhat difficult, because of the easy disproportionation of H_3GeBr to GeH_2Br_2 and polygermane $(\text{GeH}_2)_n$. The lighter halides (H_3GeF , Me_3GeF , Me_2GeF_2) are obtained by metathesis reactions of GeH_3I , Me_3GeBr or Me_2GeBr_2 with PbF_2 ⁹⁶. Trimethylfluorogermane is more conveniently prepared by the reaction of $(\text{Me}_3\text{Ge})_2\text{O}$ with SbF_3 ⁹⁵.



Both halogenosilanes and -germanes are volatile, and were handled by conventional vacuum line techniques. Their purity was initially confirmed by ^1H n.m.r. and i.r. spectra. Further confirmation of their purity and structural properties were obtained from their ESCA spectra. The binding energies of all the atoms in these species are discussed elsewhere^{74-79,87}, and mention is made here only on the general trends of the binding energies within the series $\text{Me}_n\text{H}_{3-n}\text{MX}$. Halosilanes and methylhalosilanes have been studied

by ESCA 75,76,87, some very interesting results have been obtained by these workers, for example, as methyl groups are replaced by halogen atoms, there is a stepwise increase in the binding energy. In the case of the iodides the observed increases of binding energies are less apparent due to a lack of the number of volatile samples available and to sample impurities. In substituting halogens for methyl groups there was a shift of charge from the Me_nM -moiety towards the halogen. This decreased the electron density and increased the binding energy. It has also been found that the hydrogen atom has the ability to behave as a weakly electronegative halogen. X-ray photoelectron spectroscopy may also be utilized as a method for fingerprinting, since each element, except for hydrogen, has a certain energy range by which it may be detected.

REFERENCES

1. D. P. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y. (1969).
2. A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y. (1953).
3. R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds", J. Wiley, New York, N.Y. (1948).
4. W. L. Jolly, "Synthetic Inorganic Chemistry", Prentice-Hall (1960).
5. T. Wentink and V. H. Tiensu, J. Chem. Phys., **28**, 826 (1958).
6. D. F. Van de Vondel, G. P. Van der Kelen, and G. Van Hooydonk, J. Organometal. Chem., **23**, 431 (1970).
7. H. Schmidbaur and I. Ruidisch, Inorg. Chem., **3**, 599 (1964).
8. J. R. Durig, K. K. Lau, J. B. Turner and J. Bragin, J. Mol. Spectrosc., **31**, 419 (1969).
9. J. Goubeau and H. Sommer, Z. Anorg. Allgem. Chem., **289**, 1 (1957).
10. H. Murata and S. Hayashi, J. Chem. Phys., **19**, 1217 (1951).
11. E. A. V. Ebsworth and S. G. Frankiss, Trans. Faraday Soc., 1574 (1967).
12. V. F. Mironov and N. A. Chumaevskii, Dokl. Akad. Nauk. SSSR, **146**, 1117-20 (1962).
13. J. Schraml and V. Chvalovsky, Collection Czech. Chem. Commun., **31**, (2), 503-14 (1966).
14. A. L. Smith, Spectrochim. Acta, **19**, 849 (1963).
15. A. N. Egorochkin, M. L. Khidekel, V. A. Ponomarenko, G. Ya Zueva and G. A. Razuvaev, Izv. Akad. Nauk. SSSR, 347 (1964).
16. J. W. Straley, C. H. Tindal and H. H. Nielsen, Phys. Rev., **62**, 161 (1942).

17. E. A. V. Ebsworth, S. G. Frankiss and A. G. Robiette, J. Mol. Spectrosc., 12, 299 (1964).
18. R. Řericha, J. Štokr, M. Jakoubkova, P. Svoboda and V. Chvalovsky, Collection Czech. Chem. Commun., 39, 1303 (1974).
19. C. C. Cerato, J. L. Lover and H. C. Beachell, J. Chem. Phys., 22, 1-5 (1954).
20. Kazuhiro Shimizu and Hiromu Murata, J. Chem. Soc. Japan, Pure Chem. Sect., 77, 343-6 (1956).
21. Teruo Yukitoshi, Hiroshi Suga, Syuzo Seki and Junkichi Itoh, J. Phys. Soc. Japan, 12, 506-15 (1957).
22. R. H. Pierson, A. N. Fletcher and E. S. C. Gantz, Anal. Chem., 28, 1218 (1956).
23. A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd Ed., Longmans, London, 182 (1959).
24. G. R. Waitkins and R. Shutt, Inorg. Synth., 2, 183 (1946).
25. A. Tian and S. Aubanel, Compt. Rend. Trav. Faculte Sci., Marseille, 1, 97 (1942).
26. J. W. Anderson, G. K. Barker, J. E. Drake and R. T. Hemmings, Syn. Org. Metal.-Org. Chem., 3(2), 125-128 (1973).
27. C. Glidewell, J. Inorg. Nucl. Chem., 31, 1303 (1963).
28. E. A. V. Ebsworth and J. J. Turner, J. Phys. Chem., 67, 805 (1963).
29. H. Schmidbaur, Chem. Ber., 97, 1639 (1964).
30. F. G. A. Stone and D. Seyferth, J. Inorg. and Nucl. Chem., 1, 112 (1955).
31. V. Bazant, V. Chvalovsky and J. Rathovsky, "Organosilicon Compounds", Vol. 1, Academic Press, New York, N.Y., 1965.

32. C. Eaborn, "Organosilicon Compounds", Butterworths, London (1960).
33. R. J. H. Voorhoeve, "Organohalosilanes Precursors to Silicones", American Elsevier Publishing Company Inc., New York, N.Y. (1967).
34. R. C. Mockler, J. H. Bailey and W. Gordy, J. Chem. Phys., 21, 1710 (1953).
35. C. Curran, R. M. Witucki and P. A. McCusker, J. Am. Chem. Soc., 72, 4471 (1950).
36. E. L. Reilly, C. Curran and P. A. McCusker, J. Am. Chem. Soc., 76, 3311 (1954).
37. D. S. Urch, J. Inorg. Nucl. Chem., 25, 771 (1963).
38. L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, J. Am. Chem. Soc., 76, 1613 (1954).
39. L. F. Cason and H. G. Brooks, J. Am. Chem. Soc., 74, 4582 (1952).
40. J. Cudlin and V. Chvalovsky, Coll. Czech. Chem. Comm., 28, 3088 (1963).
41. J. Knížek, M. Horak and V. Chvalovsky, Coll. Czech. Chem. Comm., 28, 3079 (1963).
42. V. Chvalovsky, Pure Appl. Chem., 13, 231 (1966).
43. Von G. Engelhardt and H. Kriegsmann, Z. Anorg. Allg. Chem., 328, 194 (1964).
44. W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", 117, Prentice-Hall (1970).
45. S. Cradock, E. A. V. Ebsworth and D. W. H. Rankin, J. Chem. Soc., (A), 1628 (1969).
46. H. Bürger and U. Goetze, Inorg. Nucl. Chem. Lett., 549 (1967).
47. F. Feher, G. Kuhlorsch, A. Blümcke, H. Keller and K. Lippert, Chem. Ber., 90, 134 (1957).
48. R. O. Sauer, J. Am. Chem. Soc., 66, 1707 (1944).

49. J. E. Drake, B. M. Glavinčevski, R. T. Hemmings and E. H. Henderson, Can. J. Chem., 56, 465 (1978).
50. J. E. Drake, B. M. Glavinčevski and R. T. Hemmings, Can. J. Chem., 58, 2161 (1980).
51. J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press New York and London, 69, (1972).
52. F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, New York, Rheine, 36 (1976).
53. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance For Organic Chemists", Wiley-Interscience, New York, London, Sydney, Toronto, 23 (1972).
54. E. A. V. Ebsworth, in "A. G. MacDiarmid (Ed), Organometallic Compounds of the Group IV Elements", Marcel Deker Inc., New York, N.Y., Vol. 1, (1968).
55. C. J. Attridge, Organometal. Chem. Rev., A, 5, 323 (1970).
56. P. Laszlo and P. J. Stang, "Organic Spectroscopy, Principles And Applications", Harper and Row, Publishers, New York, Evanston, San Francisco, London, (1971).
57. R. T. Hobgood, J. H. Goldstein and G. S. Reddy, J. Chem. Phys., 35, 2038 (1961).
58. S. Castellano and J. S. Waugh, J. Chem. Phys., 34, 295 (1961).
59. J. R. Cavanaugh, J. Chem. Phys., 39, 2378 (1963).
60. J. E. Drake, B. M. Glavinčevski, R. Humphries and A. Majid, Can. J. Chem., 57, 3253 (1979).
61. A. N. Egorochkin, N. S. Vyazankin and S. Ya. Khorshev, Russ. Chem. Rev., 41, 425 (1972).
62. T. A. Zakomoldina, P. G. Sennikov, V. A. Kuznetsov, A. N. Egorochkin and V. O. Reikhsfeld, Zh. Obshch. Khim., 50, 898 (1980).

63. V. D. Sheludyakov, V. N. Zhun', G. N. Turkel'-
taub, M. V. Polyakova, M. G. Kuznetsova, A. A.
Bernadskii and V. F. Mironov, Zh. Obshch. Khim.,
49, 1051 (1979).
64. R. W. Hoffman and H. Kurz, Chem. Ber., 108, 119
(1975).
65. J. W. Emsley, J. Feeney and L. H. Sutcliffe,
"High Resolution Nuclear Magnetic Resonance
Spectroscopy", Vol. 2, Pergamon Press Inc.,
New York, N.Y., 11101, 710 (1966).
66. G. Masetti and G. Zerbi, Spectrochim. Acta, 26A,
1891 (1970).
67. S. G. Frankiss, Spectrochim. Acta, 22, 295—
(1966).
68. G. Davidson, Spectrochim. Acta, 27A, 1161
(1971).
69. J. D. Odom, L. W. Hall, S. Riethmiller and J. R.
Durig, Inorg. Chem., 13, 170 (1974).
70. G. Davidson and S. Phillips, Spectrochim. Acta,
34A, 943 (1978).
71. G. M. Barrow, "The Structure of Molecules",
W. A. Benjamin Inc., New York, Amsterdam p. 71
(1963).
72. G. Herzberg, "Molecular Spectra and Molecular
Structure", II, Infrared and Raman Spectra of
Polyatomic Molecules, D. Van Nostrand Company
Inc., Princeton, New Jersey, thirteenth print-
ing, p. 167 (1968).
73. J. Tamas, K. Ujszaszy and Gy. Bujtas, Acta Chim.
Acad. Sci. Hung., 64, 305 (1970).
74. J. E. Drake, C. Riddle and L. Coatsworth, Can.
J. Chem., 53, 3602 (1975).
75. J. E. Drake, C. Riddle, H. E. Henderson and
B. M. Glavinčevski, Can. J. Chem. 54, 3876
(1976).
76. J. E. Drake, C. Riddle, B. M. Glavinčevski,
K. Gorzelska and H. E. Henderson, Inorg. Chem.,
17, 2333 (1978).

77. J. E. Drake, B. M. Glavinčevski and K. Gorzel-ska, J. Electron. Spectrosc. Relat. Phenom., 16, 331 (1979).
78. J. E. Drake, B. M. Glavinčevski and K. Gorzel-ska, J. Electron. Spectrosc. Relat. Phenom., 17, 73 (1979).
79. J. E. Drake, B. M. Glavinčevski and K. Gorzel-ska, Can. J. Chem., 57, 2278 (1979).
80. J. E. Drake, B. M. Glavinčevski, R. T. Hemmings and H. E. Henderson, Inorg. Synth., 19 (1979).
81. D. F. Ball, M. J. Buttler and D. C. McKean, Spectrochim. Acta, 21, 451 (1965).
82. H. J. Emelius, A. G. Maddock and C. Reid, J. Chem. Soc., 353 (1941).
83. H. R. Linton and E. R. Nixon, Spectrochim. Acta, 10, 299 (1958).
84. E. A. V. Ebsworth, R. Mould R. Taylor, G. R. Wilkinson and L. A. Woodward, Trans. Faraday Soc., 1069 (1962).
85. H. J. Emelius, M. Onyszchuk and W. Kuchen, Z. Anorg. Allgem. Chem., 283, 74 (1956).
86. L. Pierce and D. H. Peterson, J. Chem. Phys., 33, 907 (1961).
87. H. E. Henderson, PhD Thesis, University of Windsor (1977).
88. E. Carberry, T. Keene and J. Johnson, Inorg. Nucl. Chem., 37, 839 (1975).
89. H. Vahrenkamp and H. North, J. Organometal. Chem., 12, 281 (1968).
90. M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Naka-yima and K. Shiina, J. Org. Chem. 21, 1264 (1956).
91. R. West, F. A. Kramer, E. Carberry, M. Kumada and M. Ishikawa, J. Organometal. Chem., 8, 79-85 (1967).

92. J. W. Anderson, G. K. Barker, J. E. Drake and R. T. Hemmings, Can. J. Chem., 50, 1607 (1972).
93. G. K. Barker and J. E. Drake, Inorg. Nucl. Chem. Letters, Vol. 7, 39 (1971).
94. J. E. Griffiths, T. N. Srivastava and M. Onyszchuk, Can. J. Chem., 40, 579 (1962).
95. J. E. Drake, B. M. Glavinčevski and K. G. Rutherford, Inorg. Nucl. Chem. Letters, 15, 303 (1979).
96. J. W. Anderson, G. K. Barker, A. J. F. Clark, J. E. Drake and R. T. Hemmings, Spectrochim. Acta, 30A, 1081 (1974).
97. S. Tannenbaum, S. Kaye and G. Lewenz, J. Am. Chem. Soc., 75, 3753 (1953).
98. L. Pierce, J. Chem. Phys., 34, 498 (1961).
99. D. S. Rustad, T. Birchall and W. L. Jolly, Inorg. Synth., 11, 128 (1968).
100. S. Craddock and E. A. V. Ebsworth, J. Chem. Soc. (A), 12 (1967).

VITA AUCTORIS

Date of birth:

December 10, 1940; Athens, Greece.

Primary school:

A. Agelopoulou Greek and Armenian primary
school, Athens, Greece.

Secondary school:

Galt Collegiate Institute And Vocational
School, Cambridge (Galt), Ontario.

College:

The Western Ontario Institute Of Technology,
Windsor, Ontario.

Chemical Technology Diploma-1964.

University:

Wayne State University, Detroit, Michigan.
B.S. in Chemistry-1972.

Married:

To Armine' Doumbegdjian 1971.